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THE ALUMINUM CONTENT OF THE SOIL SOLUTION AND ITS RELATION TO SOIL REACTION AND PLANT GROWTH[1]

O. C. MAGISTAD

University of Wisconsin

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In recent years considerable attention has been given to soluble aluminum as a factor in the harmful effects of acid soils upon plant growth. It is held by some that the soil acids react with the aluminum compounds present in the soil, forming soluble aluminum salts, and that the amount of soluble aluminum salts thus formed, rather than the degree of acidity, determines largely the toxicity to plant growth. In order to gain further information on the amount of aluminum present in the soil solution of soils of different reactions and the action of aluminum on plant growth in relation to reaction, the present investigation was undertaken.

REVIEW OF LITERATURE

Aluminum in the soil solution

The amount of aluminum present in the soil solution depends on at least two factors: First, the amount and kind of aluminum compounds present in the soil, and second, the reaction. Aluminum is the third most abundant element in the earth's crust and is found in considerable quantities in all soils except certain sands and peats. The acids present in acid soils react with certain aluminum compounds producing soluble salts. The greater the acidity of the soil the more aluminum there will be in solution. The aluminum compound most readily attacked by acids, according to Mirasol (40) and Denison (18) is gibbsite. Hilgard (28), working with certain soils, found in them an excess of aluminum above that required to combine with the silica present to form kaolin. He concluded that aluminum hydroxide was present. Edwards (19) calculated from the recorded analyses of 244 clays, from various places in the United States, that 180 of them contained a higher ratio of aluminum to silica than that required for the formation of kaolin. He states that aluminum oxides must be present.

[1] Part of a thesis submitted at the University of Wisconsin in partial fulfillment of the requirements for the Degree of Doctor of Philosophy. Published with the permission of the Director of the Wisconsin Agricultural Experiment Station.

The writer wishes to express his appreciation for the helpful suggestions and criticisms tendered by Professor E. Truog, under whose general supervision the investigation was conducted.

The mineral acids present in an acid soil, which dissolve aluminum most readily are hydrochloric, nitric, and sulfuric acids. Ames and Boltz (3) report that the addition of sulfur to a soil results in a greater degree of acidity and in an increased amount of soluble aluminum sulfate. Denison (18) found that applications of sulfur may reduce the pH value of a soil to 3 or 4 and recent work by Joffe (31) indicates that reactions as low as pH 2.8 can thus be obtained. Under conditions of acidity as great as this, aluminum can easily go into solution. Ruprecht and Morse (50) and Hartwell and Pember (25) demonstrated that soils receiving ammonium sulfate as a fertilizer, gradually became more acid and that finally the soil solution contained considerable aluminum sulfate.

The most acid reaction which the nitrifying bacteria produce in the absence of sufficient bases is probably not acid enough to dissolve very much aluminum. Furthermore, Denison (18) and Whiting (60) give results which indicate that small quantities of soluble aluminum salts are toxic to the nitrifying bacteria, consequently, the first trace of aluminum nitrate to be formed would probably inhibit the formation of additional aluminum nitrate. On the other hand, Abbott, Conner and Smalley (2), in an investigation of the acid Kankakee marsh found that the soil solution contained enormous quantities of aluminum nitrate.

Mirasol (40), working with two acid silt loam soils, reported that a considerable part of the aluminum present could be removed by prolonged extraction with potassium nitrate. Denison (18), using the same soils, did not find aluminum in the soil extract which would pass through a collodion bag by dialysis. Arndt (4), Burgess and Pember (13), Kelley and McGeorge (33), and Blair and Prince (8) report the presence of aluminum in the soil solution.

Langworthy and Austen (36) have published several hundred analyses of natural waters for alumina. Aluminum was found in small quantities in all of them, and appreciable amounts were found in sulfur springs and the so-called alum springs. If our natural waters contain aluminum, it is evidence that the aluminum compounds in the soil are slightly soluble in the soil solution.

Presence of aluminum in plants

Aluminum is known to be present in the ash of most plants. Young (62) reported it to be a normal constituent of wheat and gluten in bread. Pfeffer (46), Johnson (32), Bertholet and André (7), Robinson, Steinkönig and Miller (48), Myers (42), Stoklasa (54), and Burgess and Pember (13) report the presence of appreciable amounts of aluminum in the ash of plants. Langworthy and Austen (36), in 1904, made an extensive compilation of analyses for aluminum in vegetable products and mineral waters. These data indicate that aluminum is present in all plants and many natural waters. The

amount of aluminum present, however, is usually small. In most plants the percentage of Al_2O_3 is approximately equal to that of Fe_2O_3 and considerably less than that of phosphorus.

Action of aluminum on plants

Varvarro (59) reported that aluminum oxide had an accelerating effect on the germination of corn but retarded germination in the case of kidney beans. Likewise, Micheels and De Heen (39) found that kaolin and alumina were somewhat beneficial to the germination of wheat. In studies with peas, wheat and rape, Hebert (27) noticed that aluminum sulfate was very toxic to germination. Stoklasa (55) and co-workers reported that small amounts of aluminum salts exerted a favorable influence on the germination of seeds, whereas larger amounts were toxic.

In solution cultures, Mirasol (40) noted that a 0.0001 *N* solution of aluminum sulfate had no effect on the rate of growth of barley. Stronger solutions proved toxic. Yamano (61), Kratzman (34), Miyake (41) and Stoklasa (55) found that dilute solutions of aluminum salts were not toxic, but with greater concentrations they observed a toxic action. One explanation of this is that large amounts of aluminum salts set free enough acid on hydrolysis to retard plant growth. Miyake (41) found that rice seedlings grew as well in solutions of aluminum chloride as in solutions of hydrochloric acid of the same normality. He made hydrogen-ion determinations and found that the hydrogen-ion concentration in the hydrochloric acid solution was nearly three times as great as that of the corresponding aluminum chloride solution. He therefore concluded that the aluminum ion was toxic. Gile (23) criticized Miyake's methods because Osterhout (43) had demonstrated that any single salt solution lowers the rate of plant growth.

Hartwell and Pember (25), who did pioneer work on the aluminum factor in acid soils, grew barley, corn and rye in nutrient solutions containing aluminum sulfate and in others containing sulfuric acid, and found that growth was about equal in solutions of the same normalities in the case of barley. Corn was depressed twice as much by the acid as by the aluminum salt. They found the hydrogen-ion concentration to be about four times as great in the solution of H_2SO_4 as in the one of aluminum sulfate. They therefore concluded that aluminum is toxic to barley but not to corn.

It is a known fact that growing plants usually tend to change an unfavorable reaction of a nutrient solution toward a more favorable one. Since a nutrient solution containing aluminum salts and of unfavorable reaction is changed less rapidly to a more favorable reaction than one of similar reaction but free of aluminum salts, the toxic effect ascribed to an aluminum salt may thus be at least partially due to its buffer influence in helping to maintain a higher hydrogen-ion concentration.

The nutrient solution used by Hartwell and Pember contained only 2 p.p.m. of phosphorus which is very low for a nutrient solution. Furthermore, it is

probable that some of the phosphorus was precipitated out of solution as ferric phosphate when ferric nitrate was added. Thus it may be possible that phosphorus was a limiting factor to growth in their experiments.

Soluble aluminum is toxic to plant growth because it acts on the protoplasm causing it to set, according to Szücs (57). He states that aluminum salts thicken the main root of the plant and render it impervious to nutrient solutions. Fluri (20) noticed that when aluminum is added to a nutrient solution, the rate of starch formation is decreased. With additions of glucose, however, starch formation went on at a normal rate. From this he concluded that aluminum renders the diastase inactive. Stoklasa (52) found small quantities of soluble aluminum beneficial and believed it to be a catalytic agent in photosynthesis. In a later work (56) he grew hydrophytes, mesophytes and xerophytes in nutrient solutions which contained soluble aluminum and in others which did not. He found that xerophytes took up little aluminum and were easily injured by small amounts of it. Mesophytes took up larger amounts, and hydrophytes still larger. The hydrophytes were injured least of all by soluble aluminum salts. He suggests that there may be a difference in the membranes of these plants which allows aluminum to come in more easily in one case than in another. He also found that when aluminum is taken in, it causes a coagulation of the protein. He states that such a condition allows other cations like calcium and potassium to migrate out of the cell readily.

Ruprecht (49) found iron and aluminum sulfate to be toxic to clover seedlings even in dilute solutions. Microscopical examinations showed that the stunting of the roots was due to a killing of the cells in the growing portion of the root. The tops continued to grow four to six days after a toxic effect was observed on the roots. He believed that the plant then died from lack of nourishment.

Effect of lime and phosphates on soluble aluminum

Lime applied to acid soils may be beneficial to plant growth for several reasons: it supplies calcium, it may reduce the hydrogen-ion concentration, and it may remove the toxic aluminum from the sphere of action by precipitating it. The precipitation of aluminum is caused by a decrease in acidity. In a few cases beneficial results were obtained by the application of phosphates to acid soils. Burgess and Pember assume that the increased growth is due partly to a precipitation of soluble aluminum as insoluble aluminum phosphate.

Burgess and Pember fertilized some of their plots with acid phosphate at the rate of 30 tons to the acre. On analyzing some of the barley grown thereon they found that the crop receiving the larger amount of phosphate contained the most aluminum. They explained the beneficial effect of the phosphorus by saying that probably the phosphorus combined with the aluminum within the plant and rendered it inactive or less toxic. Hoffer

and Trost (30) grew corn on six acid soils each variously treated with lime, phosphorus, and aluminum chloride. They analyzed the crop and found that calcium hydrate reduced the percentage of alumina in the crop. Corn grown on the soil receiving aluminum chloride had a greater percentage of alumina. They found, contrary to the results of Burgess and Pember, that applications of phosphorus decreased the percentage of alumina in the plant.

EXPERIMENTAL

A review of the literature shows that certain amounts of aluminum when in solution are toxic to plant growth. The amount of soluble aluminum necessary to cause toxicity has not been accurately determined nor is it known how much aluminum there is present in the soil solution at various reactions. In addition there is little data available on the specific way in which aluminum causes injury. The present investigation was undertaken to determine the amount of soluble aluminum in the soil solution at various reactions, the amount necessary to reduce plant growth, and the way in which aluminum acts upon the plant. To attack the problem, the following lines of investigation were undertaken:

1. The solubility of several common aluminum salts in water at various reactions was determined.
2. The amount of aluminum in displaced soil solutions from soils of various reactions was determined.
3. To prove that aluminum was present in the molecular or ionic state in the soil solution, dialysis experiments were performed.
4. The toxic effect of soluble aluminum in cultures at various pH values on alfalfa, barley, corn, oats, red clover, rye and soybeans was ascertained.
5. To determine whether aluminum actually entered the plant, some of the crops were analyzed.

Methods of determining aluminum

It is usually difficult to determine aluminum directly because it is hard to separate it from the iron with which it is usually associated. Iron and aluminum are quite similar in their chemistry and the solubilities of their compounds are much alike, hence, there are no good methods of precipitating one away from the other. The usual modes of procedure are: First, to precipitate iron and aluminum together as the hydroxides by means of ammonia, or second, to precipitate them together as the basic acetates. The combined precipitate is then ignited, weighed, the iron in it determined, and the amount of aluminum obtained by difference. When a large amount of iron and little aluminum are present, the method is unsatisfactory because the error in the iron determination is thrown on the aluminum and may there cause a relatively large error.

Additional troubles occur when the solution to be analyzed contains phosphorus and calcium. In such cases, on neutralization of the acid solution, iron will come down as the phosphate, and, if there is an adequate supply of

phosphorus, aluminum will do so also. Furthermore, with an excess of phosphorus, some calcium may be precipitated. With such solutions the usual method of procedure has been to add enough iron to precipitate all the phosphorus as ferric phosphate. In that case, calcium is not precipitated and does not interfere.

The writer wished to use a method in which aluminum is not determined by difference, or one in which iron would not need to be added to combine with the phosphorus present. The method of Carnot, described by Burgess (12) and Scott (51) was tried and found to be unsatisfactory. In this method, aluminum is precipitated as the neutral phosphate in a solution slightly acid with acetic acid while iron is reduced and kept in solution as ferrous phosphate.

The method of Carnot seems to have worked in a satisfactory manner in the hands of Pellet and Fribourg (45) for the determination of relatively large amounts of aluminum. The author, however, found that it was difficult to adjust the acidity so that precipitation of ferrous phosphate would be completely prevented while at the same time aluminum phosphate would be completely precipitated. Burgess also mentions this fact.

TABLE 1

Solubility of calcium, at various pH values, in a solution containing phosphates

pH VALUE	CaO IN SOLUTION
	p.p.m.
9.80	17.7
7.34	44.2
6.68	88.4
6.46	176.8
6.25	265.2
6.13	353.6

The method finally adopted by the writer, was to precipitate both aluminum and iron together as the phosphates at about pH 5.0. Any silica present was volatilized by hydrofluoric acid. The combined precipitates were weighed, then dissolved in acid; the amount of iron was determined colorimetrically, and the amount of aluminum secured by difference. Since iron was usually present in very small amounts, and since the thiocyanate colorimetric determination of iron is very delicate, analyses for aluminum by this method gave very good results.

Precipitation was effected at about pH 5.0 to insure a good separation between aluminum and calcium. This reaction was obtained by adding 5 cc. of acetic acid and 10 drops of 0.04 per cent brom thymol blue to about 300 cc. of solution and titrating with 1:5 ammonia to a deep blue color. This corresponds to a pH value of about 4.6. An additional 4 cc. of ammonia brought the reaction to about pH 5.0. At this reaction aluminum phosphate is completely insoluble while calcium even in a solution containing phosphates, will not be precipitated. Table 1 gives the solubility of calcium, in

parts per million CaO, at various reactions, in a solution containing 1390 p.p.m. phosphorus pentoxide introduced as sodium dihydrogen phosphate.

These data, plotted in figure 1, show that to effect a good separation between aluminum and calcium, the precipitation should be conducted at about pH 6.0 or less.

It was found that by precipitating aluminum as the phosphate at pH 5.0, one part of alumina could easily be separated from 100 parts of calcium oxide in a double precipitation.

In an attempt to determine how acid a solution might be without danger of having incomplete precipitation of aluminum phosphate, the author determined the solubility of aluminum phosphate in a solution of acetic acid

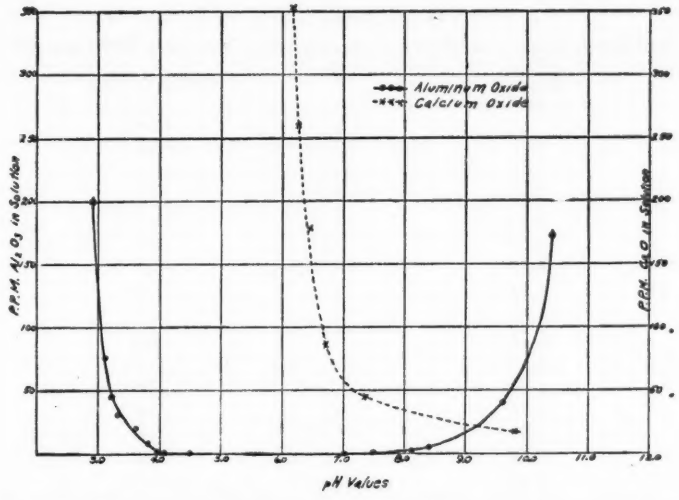

FIG. 1. CURVES SHOWING THE SOLUBILITY IN PARTS PER MILLION OF ALUMINUM OXIDE AND CALCIUM OXIDE IN A SOLUTION CONTAINING 1390 P.P.M. P_2O_5, AND AT THE pH VALUES INDICATED

at various pH values. The data of this experiment were obtained in the following manner: A definite quantity of aluminum sulfate was put into 500-cc. volumetric flasks. To each was added 5 cc. of acetic acid and the solutions were diluted to about 400 cc. Then a solution of sodium dihydrogen phosphate was introduced and dilute sodium hydroxide was added to reach approximately the desired pH values. At this point the solutions were diluted to 500 cc. and after being well shaken their pH values were determined electrometrically. Aluminum sulfate and sodium dihydrogen phosphate were used in such amounts that there were 200 p.p.m. Al_2O_3 and 1390 p.p.m. P_2O_5 in the final solution. After standing several days the supernatant liquid was perfectly clear. In each case, 100 cc. of this was then

withdrawn with a pipette and analyzed for aluminum by precipitation as aluminum phosphate at a pH value of about 5.0. The precipitate was washed and ignited as recommended by Lundell and Knowles (38).

As the precipitate of aluminum phosphate would not settle well in alkaline solutions, it was necessary to filter the slightly cloudy solution through Pasteur-Chamberland filters. The filters were prepared by ignition at 600°C. for several hours in an electric muffle. They were then digested with acid and washed till conductivity water, on passing through the filter, contained not more than 0.2 p.p.m. Al_2O_3 as determined by Atack's (5) Alizarin S colorimetric method for aluminum. The first 100 cc. of solution passing through the filter was discarded and the second 100 cc. of solution was used for analysis.

TABLE 2

Solubility of Al_2O_3 in a solution at various reactions and containing 1390 p.p.m. P_2O_5

pH VALUES	Al_2O_3 IN SOLUTION
	p.p.m.
2.86	200.0
3.11	76.4
3.19	46.0
3.33	29.6
3.58	18.0
3.79	8.7
3.95	5.8
4.07	2.5
4.29	1.5
4.50	0.3
4.95	0.0
6.84	0.0
6.97	0.0
7.49	1.8
8.10	2.1
8.42	3.7
9.58	39.5
10.40	173.0

Previous tests had shown that under similar conditions, the pH value of the second 100-cc. portion of solution passing through the filter, determined electrometrically, was practically the same before and after filtration. It was essential that the pH value of the solution did not change in filtration.

Table 2 contains data showing the solubility of aluminum phosphate at different reactions.

The data presented in table 2 were plotted in a curve shown in figure 1. This curve shows that if aluminum is precipitated at a pH value below 4.5 or above 7.0 there is a marked loss due to the solubility of aluminum phosphate.

To test the accuracy of this curve, analyses of aluminum solutions were made, precipitating the aluminum as the phosphate, at various pH values.

The pH value in each instance was determined colorimetrically by comparison with standard buffer solutions made according to the directions of Clark (15) and checked against the hydrogen electrode. The results obtained are found in table 3.

These data, when plotted as in figure 2, indicate that when the precipitation was conducted at a pH value less than 4.5, incomplete precipitation of aluminum phosphate usually took place. These data are in accord with the curve for solubility of aluminum phosphate as given in figure 1.

Analyses were made to test the accuracy of the method on solutions containing iron in addition to aluminum. The results are given in table 4.

To test further the accuracy of the method, analyses of soil solutions were made. One part of a neutral soil was well shaken with 5 parts of water and filtered. Upon analysis the filtrate was found to be free of aluminum. Varying known quantities of aluminum were added to aliquots of this extract, which were then analyzed to determine the accuracy of the foregoing method

TABLE 3

Recovery of aluminum as phosphate when precipitation was made at various pH values

The equivalent of 0.0120 gm. aluminum phosphate was used

pH VALUE AT WHICH PRECIPITATION WAS MADE	WEIGHT OF $AlPO_4$ RECOVERED
	gm.
5.6	0.0120
5.0	0.0120
4.5	0.0120
4.3	0.0119
4.2	0.0118
4.0	0.0120
3.8	0.0115
3.4	0.0086

in recovering the added aluminum by precipitation as aluminum phosphate. The results are given in table 5.

These analyses indicate that for small amount of aluminum the method is very nearly accurate.

Lundell and Knowles (38) state that this method is accurate for amounts of aluminum ranging from 1 to 5 mgm. They state that one should have present 7 to 10 times the theoretical amount of phosphate necessary for precipitation. For a greater amount of aluminum the method is less accurate because aluminum does not unite with phosphorus under all conditions strictly in the proportion of one Al_2O_3 to one P_2O_5.

After the writer had used the method for several months, he found that a committee on research and analytical methods for phosphate rock (16) had advocated the same general method for the determination of aluminum in phosphate rock. They advocated the use of methyl orange as an indicator, precipitation to be made at the point where methyl orange just turns pink.

By this method, precipitation is made at approximately pH 4.4; a reaction at which aluminum phosphate has a solubility of less than 1 p.p.m. This slight solubility would not interfere with any but the most exact work.

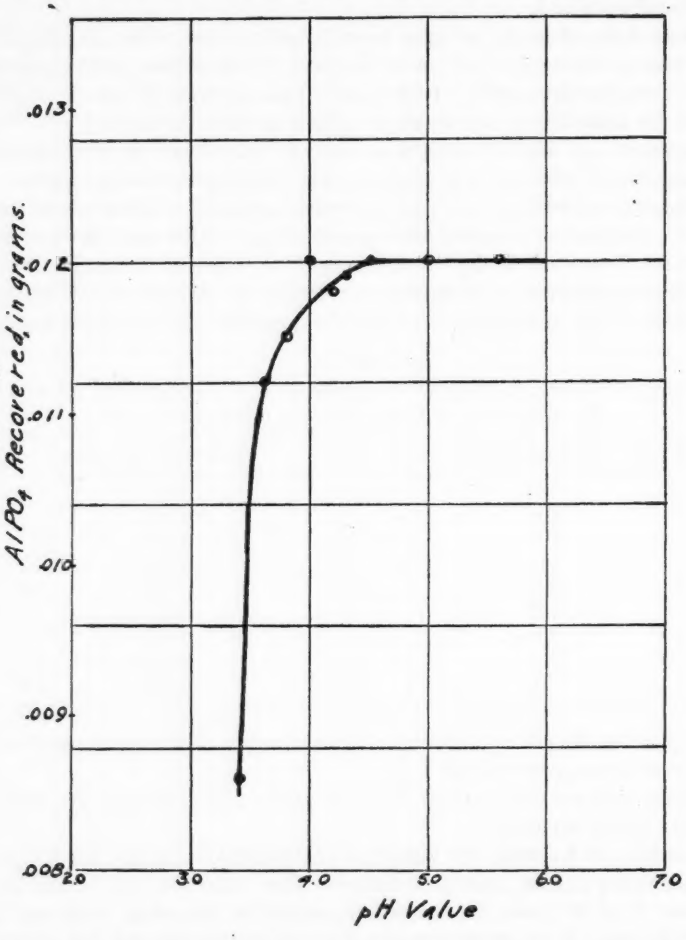

FIG. 2. CURVE SHOWING THE RECOVERY OF Al_2O_3 BY PRECIPITATION AS ALUMINUM PHOSPHATE AT DIFFERENT pH VALUES

Complete precipitation gives 0.012 gm. $AlPO_4$

Solubility of aluminum oxide in water

Soluble aluminum is found in the soil solution of acid mineral soils probably largely in combination with nitric, hydrochloric, or sulfuric acids. These

salts hydrolyze readily to form aluminum hydroxide and the corresponding acids. The writer wished to determine how much aluminum would remain unhydrolyzed in the presence of one of these acids at any given pH value in water solution. Such data may probably indicate the maximum amount of aluminum present in the soil solution at any particular reaction.

The data were obtained in the following manner. A definite quantity of aluminum sulfate was put into each of several 500-cc. volumetric flasks and each diluted to approximately 400 cc. Due to hydrolysis these solutions were distinctly acid. Then sodium hydroxide, made from metallic sodium, was added to reach the desired pH values. The solutions were diluted to 500 cc. and after repeated shaking their pH values were determined electro-

TABLE 4

Result of analysis for aluminum by the method used by the writer, in a solution containing 2 mgm. of Al_2O_3 and some iron

	a	b
	gm.	*gm.*
Weight of combined precipitates	0.0123	0.0120
Weight of $FePO_4$ as calculated from the weight of Fe_2O_3 found	0.0073	0.0073
Weight of $AlPO_4$ found	0.0050	0.0047
Theoretical weight of $AlPO_4$ taken	0.0048	0.0048

TABLE 5

Recovery of aluminum as phosphate, in a soil extract to which known amounts of aluminum had been added

Al_2O_3 ADDED	Al_2O_3 RECOVERED
gm.	*gm.*
0.00030	0.00029
0.00030	0.00026
0.00100	0.00096

metrically. Upon standing several days the supernatant liquid usually became very clear. In each case, 100 cc. of this supernatant liquid was withdrawn with a pipette for analysis to ascertain the amount of aluminum in solution at that particular pH value. With the addition of large quantities of sodium hydroxide, the reaction became alkaline and the aluminum went into solution as sodium aluminate. In alkaline reactions the undissolved aluminum did not settle readily and the solutions were consequently filtered through Pasteur-Chamberland filters.

The solutions were analyzed for aluminum by precipitation as phosphate except in the case of the range between pH 4.6 and 7.5 where only very small amounts of aluminum were in solution. Here the colorimetric method of Atack (5), by means of Alizarin S, was used because of its convenience and

greater accuracy for very small amounts. The writer has found Alizarin S to be a good qualitative test for aluminum and also a good quantitative method for the determination of small amounts of aluminum when iron and phosphorus are absent, or present in very small quantities. The data giving the solubility of aluminum oxide in water at various pH values are found in table 6.

The data in table 6 were also plotted in a curve in figure 3. This curve indicates that only small quantities of aluminum can exist in solution between pH 4.7 and about pH 7.8. The region of greatest insolubility lies between

TABLE 6

Solubility of aluminum in water at the indicated pH values

pH VALUE	Al_2O_3 IN SOLUTION
	p.p.m.
3.92	1000.0
3.94	600.0
3.95	400.0
3.96	200.0
4.02	130.0
4.19	79.0
4.27	43.0
4.51	6.5
4.66	2.3
5.22	1.2
5.40	0.8
5.62	0.7
6.00	0.4
6.80	0.3
7.00	0.4
7.55	2.0
8.35	8.4
8.95	34.6
9.28	63.4
9.48	124.0
9.75	200.0
10.10	400.0
10.15	600.0
10.43	1100.0

pH 5.8 and pH 7.0. Blum (9), in his research regarding the reaction at which aluminum can best be precipitated by ammonia, found that aluminum hydroxide has its greatest insolubility between pH 6.5 and 7.5. He advocates precipitation of aluminum hydroxide at pH 6.5 using methyl red as an indicator. Hatfield (26) determined the amount of aluminum in the effluent from sludge which had been coagulated with alum and filtered at various pH values. He used the hematoxylin colorimetric test and found that the region of greatest insolubility of aluminum was from pH 5.7 to pH 7.3. Buswell and Edwards (14) treated various waters with alum, analyzed the fil-

trate for aluminum, and found that the amount of aluminum in the filtrate varied from about 0.4 p.p.m. at pH 6.0 to 2.0 p.p.m. at pH 8.0.

Banerji (6) investigated the question of flocculation of colloidal material in certain Indian rivers by means of aluminum sulfate. Best clarification was obtained at pH 6.5 to 7.5. It is held by some that alum clarifies alkaline waters due to a change in reaction in which the sulfuric acid, arising from hydrolysis of the aluminum sulfate, changes the reaction nearer the iso-electric point of the suspended soil particles. Furthermore, the aluminum sulfate on hydrolysis yields aluminum hydroxide, a precipitate that settles and carries down with it the finely divided suspended matter. Banerji

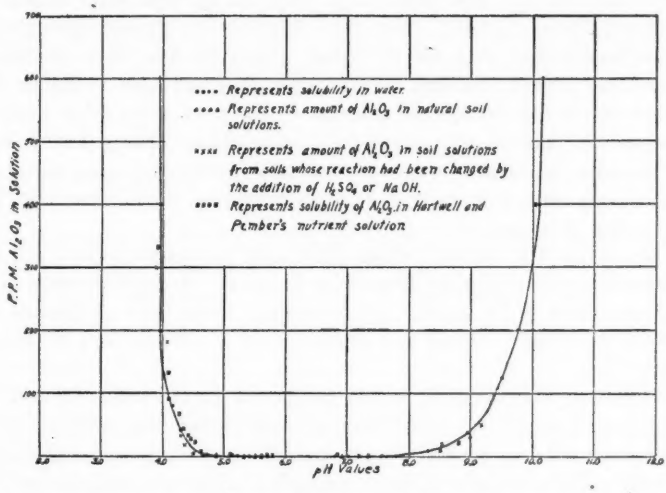
•••• Represents solubility in water
•••• Represents amount of Al_2O_3 in natural soil solutions.
•••• Represents amount of Al_2O_3 in soil solutions from soils whose reaction had been changed by the addition of H_2SO_4 or NaOH.
•••• Represents solubility of Al_2O_3 in Hartwell and Pember's nutrient solution
P.P.M. Al_2O_3 in Solution
pH Values

FIG. 3. CURVE SHOWING THE PARTS PER MILLION OF Al_2O_3, IN SOLUTION IN WATER, AT pH VALUES INDICATED

Solubility in other solutions at pH values indicated is also represented

found pH 6.7 as the iso-electric point of aluminum hydroxide; at reactions more alkaline or acid it tended to redissolve.

The amount of aluminum which can exist in solution is markedly increased when the reaction becomes more acid than pH 4.7 or more alkaline than pH 8.5. In dealing with the amount of soluble aluminum present in the soil solution and in nutrient solutions, further reference will be made regarding the curve for the solubility of aluminum hydroxide in water.

Aluminum in the soil solution

The author wished to determine the amount of aluminum actually present in the soil solution, since it is usually conceded that toxic substances must be in solution to affect the growth of a plant. If only minute quantities of

aluminum, quantities too small to be toxic, are in solution at any particular time, then no matter how big the reserve of easily soluble aluminum, there cannot be any toxic action.

Soil solutions were obtained by alcohol displacement according to the method described by Parker (44). Large glass percolators were used instead of brass cylinders because salts in the soil would react with the latter to a slight extent producing soluble copper salts.

Soil solutions obtained from acid soils came through clear and were not filtered prior to analysis. The percolate from alkaline soils contained organic matter and finely divided clay. These solutions were filtered through Pasteur-Chamberland filters. The filters were prepared as previously indicated. The second 50-cc. portion of percolate obtained was filtered through the Pasteur-Chamberland filter and discarded. Then the first 50-cc. portion of percolate was filtered and used for analysis. This was done to insure that the filter would not change the reaction of the portion used for analysis. It was essential that the pH value of the solution did not change during filtration, for, since the solution was saturated with aluminum at that particular pH value, any change in reaction towards neutrality would have caused a precipitation of aluminum.

To the acid soil solutions, sodium dihydrogen phosphate was added, and the aluminum and iron were determined as usual. A double precipitation was always made in the case of soil solutions. In the case of alkaline soil solutions, the organic matter was destroyed by nitric acid and potassium chlorate.

Soil solutions were obtained from a number of natural soils. In addition soil solutions were also obtained from soils which had been made acid and alkaline artificially by adding varying amounts of sulfuric acid and sodium hydroxide. The soils used for this work were a Miami silt loam, a Plainfield fine sandy loam, and a Waukesha silt loam. The reagent was well mixed with the soil which was then kept at the optimum moisture content and remixed at 3-day intervals to insure thorough mixing.

Soon after the acid was added, determinations indicated a reaction of pH 2.0 to 3.0. On succeeding days the pH values gradually increased till at the end of about two weeks the difference in pH values, determined at 3-day intervals, was less than 0.02 of a unit. At this stage the reactions were considered constant and the soil solutions then displaced.

The amounts of aluminum found in soil solutions at varied reactions are given in tables 7 and 8.

These data are also plotted in figure 3. From this figure it is evident that the curve showing the amount of aluminum present in the soil solution at various reactions is nearly identical with the curve showing the solubility of aluminum sulfate in water at various pH values. Since the two curves practically coincide, one can predict with a fair degree of certainty the amount of soluble aluminum present in a soil solution on knowing the pH value of

the soil. Thus it becomes evident that amounts of soluble aluminum greater than 3 p.p.m. can exist in a soil only when the reaction is more acid than pH 4.7 or more alkaline than about pH 8.0. From pH 5.4 to 7.0 the amount of aluminum present in solution is usually less than one part per million.

Significant in this connection is the work of Aarnio (1) on certain peat soils of Finland. He found no soluble aluminum in soil sections having a pH of about 6.0. Traces were found at pH 5.7 and considerably larger

TABLE 7

Aluminum present in the soil solution of natural soils at the indicated pH values

pH VALUE	Al_2O_3
	p.p.m.
4.87	1.2
5.14	2.0
5.30	0.7
5.50	0.3
6.90	0.7
9.01	31.0

TABLE 8

Aluminum in the soil solution of soils made acid and alkaline with sulfuric acid and sodium hydroxide respectively

SOIL TYPE	pH VALUE	Al_2O_3
		p.p.m.
Miami silt loam	3.29	1860.0
Waukesha fine sandy loam	3.68	597.0
Miami silt loam	3.72	351.0
Miami silt loam	3.92	297.0
Plainfield fine sandy loam	4.06	182.0
Plainfield fine sandy loam	4.30	33.0
Miami silt loam	4.35	19.0
Miami silt loam	4.50	3.0
Plainfield fine sandy loam	4.64	1.4
Waukesha fine sandy loam	5.78	1.9
Miami silt loam	7.21	0.0
Waukesha fine sandy loam	7.33	0.4
Miami silt loam	8.52	19.0
Miami silt loam	8.95	37.6
Miami silt loam	9.17	48.0

amounts at pH values below 4.8. This work is in perfect harmony with the curve in figure 3.

The work reported from the Rhode Island station (25) was done on soils having a pH value of 4.7. If the pH values were determined colorimetrically the accuracy would probably be within 0.2 or 0.3 of a unit. At a slightly lower pH value than 4.7 it is possible, on the basis of the curve in figure 3 to have as much aluminum in solution as is reported in these experiments.

It might be contended that the organic acids of soils would form considerable amounts of soluble aluminum salts which would remain in solution at pH values greater than 4.7. It is true that some organic acids do prevent the precipitation of aluminum at slightly acid reactions. For example, 200 p.p.m. of aluminum acetate in water at ordinary temperatures will not be precipitated at pH 5.4 even on prolonged standing. The presence of simple organic acids such as formic, acetic and propionic acids in soils has been demonstrated by Pierre (47), Kröber (35), and Stoklasa and Ernst (52).

It is improbable, however, that sufficient amounts of these acids can long exist in the soil because they are quickly attacked by bacteria and molds as indicated by Löhnis (37). Stoklasa and Ernst (53) state that these simple organic acids are easily oxidized by bacteria to CO_2 and water.

The curve showing the solubility of aluminum in the soil solution indicates low solubilities at reactions between pH 4.7 and 8.5, even with soils containing considerable organic matter. The results indicate that in mineral soils the amount of organic acids present, capable of keeping aluminum in solution, is negligible as far as this problem is concerned.

Mirasol (40) believed that gibbsite was present in ordinary soils and that it was the form of aluminum most readily attacked by the soil acids. To obtain evidence upon this subject, the writer obtained colloidal material from three soils and submitted them to Professor W. J. Mead of the department of geology University of Wisconsin for X-ray analysis. The samples were prepared as follows:

> Three 25-gm samples of soil were placed in flasks and each was well shaken with 500 cc. of water. The flasks were then allowed to stand 20 minutes, after which 100 cc. of the supernatant liquid was removed with a pipette and evaporated to dryness. The powder thus obtained was used for analysis.

The soils used were a Miami silt loam, a Carrington silt loam, and a Baxter silt loam. The last named is a residual soil while the first two are of glacial origin.

Upon analysis the lines upon the plates were found identical with those of quartz. Only in the case of the Baxter silt loam were additional lines present. These were very faint and few in number indicating that only a small amount of the material giving rise to them was present. The analyses showed conclusively that silicon dioxide was the principal crystalline material in the finely divided matter of the soils studied.

It is very probable, however, that were gibbsite present it would be in the amorphous state. Since the X-ray method does not indicate the presence of amorphous material, the results obtained were not conclusive evidence as to the absence of gibbsite in these soils.

Dialysis experiments

Denison (18) believed that aluminum is present in the soil solution as a hydrogel of aluminum hydroxide, which does not dialyze through collodion

bags. It seems that if aluminum were present in the soil solution in colloidal form instead of in true solution, it would have difficulty in getting into the plant and causing injury.

Clear soil solutions were obtained by alcohol displacement from soils made acid by sulfuric acid as previously explained. When exposed to a strong beam of light, however, they exhibited a Tyndall cone proving that colloidal material was present. Filtration through Pasteur-Chamberlain filters removed only a portion of the colloidal material.

Such a solution was dialyzed through a collodion bag for 6 days. The outside water was removed every 12 hours and fresh conductivity water added. The diffusate was evaporated to dryness in platinum dishes and analyzed for aluminum. In addition the collodion bag and its contents were analyzed for aluminum at the end of the experiment. The analyses showed that the original soil solution contained 297 p.p.m. of aluminum oxide all of which dialyzed through the bag. The bag and its contents at the end of the experiment contained no aluminum. A careful test of the water itself showed that it did not contain aluminum. Saturated solutions of aluminum sulfate in water at various reactions were analyzed to obtain data for solubility curves. Upon examining one of these solutions, no Tyndall cone was visible. The solution was then dialyzed in the same way as the soil solution and of the total 768 p.p.m. aluminum oxide present, 765 p.p.m. dialyzed through the bag. The bag and contents at the end of the experiment contained the equivalent of 3.0 p.p.m. aluminum oxide.

Because the solutions which were analyzed to determine the solubility curve of aluminum sulfate in water contained so very little colloidal aluminum, and because the curve for the solubility of aluminum in soil solutions is nearly identical with it, it can be reasonably inferred that the aluminum in question, present in the soil solution, must be in the molecular or ionic state.

The writer regrets that he has not been able to obtain a natural soil sufficiently acid to contain amounts of aluminum in the soil solution large enough for dialysis experiments.

The soil solution of a natural alkali soil from Fresno, California, was obtained by alcohol displacement. The percolate was colored, but on visual inspection did not seem to contain any colloidal inorganic matter. It was not filtered, but was at once dialyzed for 5 days. The combined diffusate was analyzed and found to contain 31 p.p.m. aluminum oxide on the basis of the weight of the original soil solution. The bag and contents contained 12.5 p.p.m. alumina. The pH of the soil solution determined electrometrically was 9.01. It will be seen from figure 3 that at this reaction the solution should contain about 30 to 35 p.p.m. aluminum oxide.

It was noted by the writer that nearly all of the colored material present in the soil solution dialyzed through the collodion bag, indicating that the organic matter was also in true solution.

These experiments indicate that the aluminum found in the soil solution

of acid and alkaline soils is present largely in true solution and in that state it is no doubt able to enter the plant roots.

Greenhouse experiments

Greenhouse experiments were conducted to determine the toxicity of aluminum to plants at various pH values. The plants grown were alfalfa, barley, corn, oats, rye, red clover and soybeans.

Some of the previous experiments on aluminum toxicity can be criticized because the plants were grown at reactions as low as pH 2.9 to 4.1 and no higher. A range of reaction as acid as this is seldom encountered under field conditions, and it is probably so acid that some of the plant organs do not function properly, and the results obtained are untrustworthy. In order to test whether or not aluminum is toxic, the plants should be grown in as near normal conditions as possible as far as other factors are concerned. This means that the reaction should be as near to neutrality as will still permit the aluminum to remain in solution.

TABLE 9

Solubility of aluminum sulfate, in Crone's nutrient solution at the pH values indicated

pH VALUE	Al_2O_3 IN SOLUTION
	p.p.m.
4.50	1.7
3.60	20.0
3.50	51.4
3.45	79.5

Aluminum salts when introduced into a nutrient solution may hydrolyze, setting free an acid. Plants grown in a nutrient solution of this kind may then be affected by two harmful conditions; the acid reaction and the presence of aluminum. In order to determine the toxicity of aluminum alone, it is necessary to grow plants in two series of cultures; one containing aluminum salts and the other containing enough acid so that the respective reactions in the two series are equal. Thus, a poor growth in a culture containing aluminum sulfate at pH 4.2 as compared with the growth in a culture containing sulfuric acid at pH 4.2 indicates a toxicity due to aluminum.

Crone's nutrient solution (21) has been found to be an excellent one for greenhouse work. It contains about 20 p.p.m. of phosphorus. Determinations were made on the solubility of freshly precipitated aluminum hydroxide in this solution at various reactions. The results are given in table 9.

These data, plotted in figure 4, indicate that the amount of aluminum present in Crone's nutrient solution is small at acidities less than pH 3.6. This is undoubtedly due to the high phosphorus content. Consequently, were this solution used for greenhouse work, it would be necessary to keep the pH value below 3.6 in order that the solution might contain more than

moderate amounts of Al_2O_3. It is thus not adapted for use in this investigation.

Determinations were made of the solubility of aluminum sulfate in Hartwell and Pember's (25) nutrient solution at various reactions. The reaction was in each case determined colorimetrically and the amount of aluminum was determined as in the previous experiments. The results are shown in table 10.

These data are plotted in figure 3, which shows that the curve for the solubility of aluminum hydroxide in Hartwell and Pember's nutrient solution at various reactions practically coincides with the curve giving the solubility of aluminum hydroxide in water at the same reactions, although

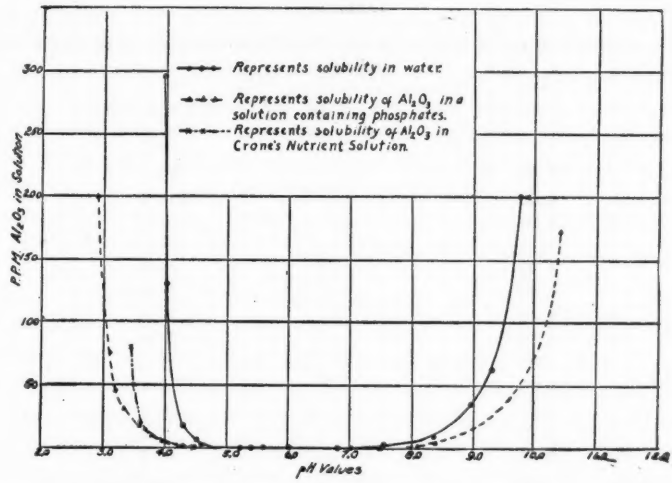

FIG. 4. CURVES SHOWING THE PARTS PER MILLION OF Al_2O_3, IN SOLUTION IN WATER, IN CRONE'S NUTRIENT SOLUTION AND IN A SOLUTION CONTAINING PHOSPHATES, AT pH VALUES INDICATED

around pH 4.5 the solubility in the nutrient solution seems to be somewhat higher. The solubility of aluminum in Hartwell and Pember's nutrient solution is also practically the same as in the soil solution at the same reaction; consequently, as regards the amount of aluminum present and the reaction, this nutrient solution duplicates natural soil conditions, and hence was used with certain modifications that are later explained.

The plants were grown in Ottawa silica sand cultures which had been digested with hydrochloric acid and washed. Glass percolators were used as containers, some having a capacity of 2 liters and others of 700 cc., and were provided with a stopcock at the bottom to facilitate removal of the old solution which was done by suction, twice daily.

The plan of the experiment was to grow plants in two series at various reactions, one series to have aluminum present and the other series not to have aluminum present. In the experiment with alfalfa, barley and rye, the series consisted of cultures at pH 4.0, 4 2, 5.0, 6.0, 7.0, 8.0, 9.0, and 9.5 except in the case of alfalfa where the cultures at pH 8.0 and 9.5 were omitted. The amounts of alumina present in solution in the nutrient solutions at these reactions were 100.0, 50.0, 3.0, 0.4, 0.4, 5.0, 40.0 and 100.0 p.p.m. respectively.

The nutrient solutions were brought to the desired reaction by the addition of sulfuric acid or sodium hydroxide. No buffer was used at reactions below 6.0. At pH 9.0 and 9.5 sodium carbonate was used as a buffer at the

TABLE 10

Solubility of aluminum sulfate in Hartwell and Pember's nutrient solution at the pH values indicated

pH VALUE	Al_2O_3 IN SOLUTION
	p.p.m.
3.90	336.0
4.05	134.0
4.20	96.0
4.25	69.7
4.30	46.0
4.40	29.0
4.45	24.6
4.50	23.0
4.60	7.5
5.10	3.0
5.70	0.5
6.80	3.0
8.50	10.8
8.80	21.7
10.00	400.0

rate of $\frac{3}{4}$ gm. per liter. At pH values between 6.0 and 9.0 sodium bicarbonate was used at the same rate. The sand used had little if any buffer material present after being digested with hydrochloric acid. Throughout the work the deviation in reaction of the solution in any percolator was less than one unit from the desired mean. In the case of the cultures at pH 4.0, 4.2, 9.0 and 9.5 the maximum deviation was 0.6 of a unit but usually the deviation was less than 0.4 of a unit. The composition of Hartwell and Pember's nutrient solution used[2] was as follows:

[2] In addition to this nutrient solution, in all but the first experiment, additional phosphorus was supplied by mixing ferric phosphate and tri-calcium phosphate with the culture medium as later explained.

SALT	GRAMS PER LITER
$Ca(NO_3)_2 \cdot 4H_2O$	0.3543
NH_4NO_3	0.0801
KCl	0.0597
$MgSO_4 \cdot 6H_2O$	0.1972
$CaH_4(PO_4)_2 \cdot H_2O$	0.0083
$Fe(NO_3)_3 \cdot 9H_2O$	0.0200

For alfalfa, the nutrient solution was modified by omitting nitrogen salts and by adding an equivalent amount of ferric chloride and calcium sulfate in place of ferric nitrate and calcium nitrate respectively.

Preliminary experiments under these conditions with alfalfa, barley and rye indicated that aluminum, when dissolved in the nutrient solution in amounts greater than 10.0 p.p.m., was decidedly toxic to the growth of alfalfa and barley and to a lesser extent to rye. Good growth was not obtained in the cultures without aluminum at optimum reactions, which indicated that some other factor was limiting growth. An inadequate supply of phosphorus was suspected to be the cause of it, since the nutrient solution contained only 2 p.p.m. of phosphorus. In the experiments which follow, to overcome this deficiency, sufficient ferric phosphate was mixed with the sand to give 0.0065 per cent phosphorus. Truog (58) has shown that barley and some other crops can make good growth using ferric phosphate as the only source of phosphorus. The ferric phosphate served as a constant supply of phosphorus available to the plant; furthermore, phosphorus in this form did not cause precipitation of the aluminum present in the solution or change the reaction, as would be the case if more of a soluble phosphate were added.

At pH values above 6.0 it was feared that ferric phosphate is too insoluble and hence in addition to the ferric phosphate, an equivalent amount of tri-calcium phosphate was mixed with the sand. Above pH 6, tri-calcium phosphate does not appreciably affect the reaction. The profuse growth obtained in this experiment compared to the previous one at reactions approaching neutrality clearly demonstrated that phosphorus had been a limiting factor in the first experiment.

In an experiment with alfalfa, barley and rye, within the first week a toxic effect of aluminum occurred on alfalfa at pH 4.0, 4.2, and 9.0, and on barley at pH 4.0 and 4.2, most of the plants having died. As the experiment progressed it became clear that the region of best growth for alfalfa lay between pH 6.0 and 8.5; for barley at about 6.5 and for rye at reactions approaching neutrality.

It is possible that alfalfa will grow well at more acid reactions when nitrates are supplied. The alfalfa bacteria, however, do not grow well or live long at reactions of pH 5.0 or lower as shown by Bryan (11), and Fred and Davenport (22).

The rye and barley plants were washed out of the sand cultures 33 days

TABLE 11

Weight of dry barley roots and tops grown in sand cultures of various reactions with and without aluminum

The plants were 33 days old

pH VALUE OF CULTURE	WITHOUT ALUMINUM		WITH ALUMINUM	
	Roots	Tops	Roots	Tops
	gm.	*gm.*	*gm.*	*gm.*
4.0	0.167	0.474	0.100	0.083
4.2	0.193	0.620	0.130	0.188
5.0	0.203	0.734	0.198	0.520
6.0	0.210	1.372	0.194	1.138
7.0	0.201	1.147	0.172	1.002
8.0	0.122	0.427	0.107	0.362
9.0	0.120	0.253	0.113	0.213
9.5	0.111	Lost	0.089	0.121

TABLE 12

Weight of dry rye roots and tops grown in sand cultures of various reactions with and without aluminum

The plants were 33 days old

pH VALUE OF CULTURE	WITHOUT ALUMINUM		WITH ALUMINUM	
	Roots	Tops	Roots	Tops
	gm.	*gm.*	*gm.*	*gm.*
4.0	0.226	0.506	0.201	0.300
4.2	0.230	0.561	0.218	0.204
5.0	0.184	0.894	0.260	0.709
6.0	0.286	1.280	0.288	1.519
7.0	0.352	0.750	0.336	0.863
8.0	0.156	0.492	0.124	0.475
9.0	0.161	0.361	0.109	0.388
9.5	0.108	0.194	0.092	0.207

TABLE 13

Weight of dry alfalfa roots and tops grown in sand cultures of various reactions with and without aluminum

The plants were 65 days old

pH VALUE OF CULTURE	WITHOUT ALUMINUM		WITH ALUMINUM	
	Roots	Tops	Roots	Tops
	gm.	*gm.*	*gm.*	*gm.*
4.0	Dead	Dead	Dead	Dead
4.2	Dead	Dead	Dead	Dead
5.0	0.009	0.008	0.010	0.009
6.0	0.123	0.273	0.115	0.270
7.0	0.253	0.362	0.260	0.402
9.0	0.016	0.032	Dead	Dead

after planting. In the case of rye, there was no apparent difference between the roots of plants which received aluminum and of those which did not. In the case of barley, however, the roots of the plants in the culture at pH 4.2 receiving aluminum were short, coarse and unbranched.

The dry weights of the barley and rye plants are given in tables 11 and 12. These weights show that the amounts of aluminum present in the nutrient solutions at pH 4.0 and 4.2 are decidedly toxic to both barley and rye. It would also seem from the weight of tops that the amount of aluminum in solution at pH 5.0 is toxic. Hartwell (24) stated in this connection that 3 p.p.m. of aluminum, approximately the amount present at pH 5.0, exerts a very deleterious effect upon young lettuce plants. In this experiment as well as in the previous one rye seemed to withstand the toxic effect of soluble aluminum better than barley.

The alfalfa series was allowed to grow 65 days. All the plants at pH 4.0 and 4.2 died, but those receiving aluminum died first. The plants at pH 9.0 receiving aluminum also died. At pH 5.0 the growth was poor; at pH 6.0, fairly good; and at pH 7.0, very good. Plants were not grown at pH 8.0 but the plants at pH 9.0 without aluminum made some growth, which was better than at pH 5.0. There was no indication of aluminum toxicity at pH 5.0, 6.0, and 7.0. The weights of the dry alfalfa roots and tops are found in table 13.

In the next experiment, corn, oats, soybeans and red clover were grown. The percolators were of 700-cc. capacity and the reactions of the cultures were pH 4.0, 4.2, 4.7, 5.6, and 6.4. The reaction of the culture at pH 6.4 was obtained by adding ground limestone to the sand at the rate of 4 tons to the acre which in contact with the CO_2 in the cultures comes to equilibrium at about pH 6.4. In the case of red clover, the pH of the culture receiving ground limestone was a little higher than pH 6.4. The same nutrient solution as used in the previous experiment was used for all crops; the experiment being conducted in the same manner as the previous one with rye and barley. The soybeans and clover were inoculated with appropriate cultures soon after germination which was normal in all cases. At the time, however, the toxicity of aluminum to corn and soybeans was apparent at pH 4.0 and 4.2. Later, aluminum toxicity was noted on the oats and clover at pH 4.0 and 4.2

At the end of 32 days the corn, oats, and soybean plants were washed out of the sand cultures and pictures taken of the roots and tops. The clover plants were allowed to grow 42 days. It was noted while washing out the plants that the best root systems, in each case, occurred in the cultures receiving lime. At reactions of pH 4.0 and 4.2 the amount of aluminum present caused a stubby, unbranched root system. This was particularly noticeable in the case of corn, oats, and soybeans. Nodules were small and present on the clover and soybeans only at the least acid reaction. The weights of the dried roots and tops are given in tables 14 to 17.

TABLE 14

Weight of dry corn roots and tops grown in sand cultures of various reactions with and without aluminum

The plants were 32 days old

pH VALUE OF CULTURE	WITHOUT ALUMINUM		WITH ALUMINUM	
	Roots	Tops	Roots	Tops
	gm.	*gm.*	*gm.*	*gm.*
4.0	0.220	0.403	0.100	0.083
4.2	0.430	0.547	0.103	0.114
4.7	0.338	0.981	0.302	0.447
5.6	0.417	0.998	0.314	0.822
6.0	0.516	1.302	0.319	0.946
6.4	0.991	1.571	0.794	1.368

TABLE 15

Weight of dry oat roots and tops grown in sand cultures of various reactions with and without aluminum

The plants were 32 days old

pH VALUE OF CULTURE	WITHOUT ALUMINUM		WITH ALUMINUM	
	Roots	Tops	Roots	Tops
	gm.	*gm.*	*gm.*	*gm.*
4.0	0.269	0.414	0.174	0.153
4.2	0.300	0.473	0.182	0.194
4.7	0.320	0.571	0.285	0.368
5.6	0.351	0.751	0.356	0.726
6.0	0.416	0.824	0.364	0.753
6.4	0.420	0.838	0.431	0.862

TABLE 16

Weight of dry soybean roots and tops grown in sand cultures of various reactions with and without aluminum

The plants were 32 days old

pH VALUE OF CULTURE	WITHOUT ALUMINUM		WITH ALUMINUM	
	Roots	Tops	Roots	Tops
	gm.	*gm.*	*gm.*	*gm.*
4.0	0.219	0.913	0.102	0.242
4.2	0.236	0.930	0.201	0.723
4.7	0.325	1.389	0.250	0.894
5.6	0.301	1.401	0.247	1.057
6.0	0.277	1.490	0.251	1.167
6.4	0.421	1.464	0.448	1.647

The weights show that large quantities of soluble aluminum are decidedly toxic to the growth of these crops. At reactions approaching neutrality, the amount of aluminum in solution is so small that it does not appreciably retard plant growth. Of these four crops, corn is injured the most, followed by clover, soybeans and oats in the order named.

By introducing it as aluminum citrate and tartrate Hartwell and Pember attempted to determine whether aluminum was toxic in alkaline cultures. They found no harmful effects due to its presence but they state that the solution was cloudy, and they were not certain that the aluminum was in solution.

The writer knows of no other data bearing upon the subject of aluminum toxicity under alkaline conditions. In the first series of experiments aluminum exerted a decided toxic effect upon barley and alfalfa at pH 9.0. Again in the second series it proved toxic to alfalfa at this reaction. This suggests that soluble aluminum may be a factor in the toxicity of alkali soils.

TABLE 17

Weight of dry clover roots and tops grown in sand cultures of various reactions with and without aluminum

The plants were 42 days old

pH VALUE OF CULTURE	WITHOUT ALUMINUM		WITH ALUMINUM	
	Roots	Tops	Roots	Tops
	gm.	*gm.*	*gm.*	*gm.*
4.0	0.010	0.030	0.003	0.008
4.2	0.010	0.042	0.004	0.009
4.7	0.011	0.049	0.012	0.030
5.6	0.024	0.072	0.033	0.071
6.0	0.046	0.157	0.059	0.146
6.8	0.112	0.384	0.112	0.348

Alkali soils often have pH values above 9.0 which according to figure 3 would indicate that the soil solution contains relatively large amounts of aluminum. Rye is more resistant to aluminum injury than alfalfa or barley in acid as well as in alkaline reactions and it is particularly significant that rye is as well or better adapted to alkaline soils than many other crops.

Physiological effect of soluble aluminum on plants

The rye and barley plants grown in the first series were analyzed for iron and aluminum, the roots and tops being analyzed separately. The material after being weighed was ashed in silica dishes in an electric muffle. The ignited residue was then taken up with hydrochloric acid and the aluminum determined as the phosphate. The results of these analyses are given in tables 18 to 21.

Since the analyses reported in tables 18 to 21, inclusive, were made on very

TABLE 18

Fe_2O_3 and Al_2O_3 in barley roots grown in sand cultures with and without the addition of soluble aluminum at various reactions

pH VALUE OF CULTURE	WITHOUT ALUMINUM		WITH ALUMINUM	
	Fe_2O_3	Al_2O_3	Fe_2O_3	Al_2O_3
	per cent	*per cent*	*per cent*	*per cent*
4.0	0.45	0.06	0.13	1.52
4.2	1.17	0.07	0.19	1.96
5.0	1.50	0.16	0.13	1.29
6.0	1.26	0.04	0.06	0.98
7.0	1.98	0.21	0.08	1.43
8.0	1.06	0.41	0.06	0.69
9.0	1.92	0.50	0.07	0.42

TABLE 19

Fe_2O_3 and Al_2O_3 in barley tops grown in sand cultures with and without aluminum at various reactions

pH VALUE OF CULTURE	WITHOUT ALUMINUM		WITH ALUMINUM	
	Fe_2O_3	Al_2O_3	Fe_2O_3	Al_2O_3
	per cent	*per cent*	*per cent*	*per cent*
4.0	0.132	.....	0.029	.....
4.2	0.122	0.025	0.027	0.254
5.0	0.077	0.018	0.016	0.243
6.0	0.035	0.017	0.007	0.190
7.0	0.034	0.022	0.010	0.120
8.0	0.028	0.046	0.009	0.167
9.0	0.024	.....	0.008	0.257

TABLE 20

Fe_2O_3 and Al_2O_3 in rye roots grown in sand cultures with and without aluminum at various reactions

pH VALUE OF CULTURE	WITHOUT ALUMINUM		WITH ALUMINUM	
	Fe_2O_3	Al_2O_3	Fe_2O_3	Al_2O_3
	per cent	*per cent*	*per cent*	*per cent*
4.0	1.18	0.11	0.77	1.18
4.2	0.99	0.07	0.92	1.16
5.0	1.12	0.10	0.80	0.96
6.0	....	....	0.38	0.59
7.0	0.73	0.07	0.19	0.74
8.0	0.71	0.16	0.35	0.78
9.0	1.56	0.10	0.65	0.37

small amounts of material, the results are not so reliable as they might be. They indicate, however, that when plants are grown in sand cultures containing soluble aluminum, some of the aluminum is taken up by the plants. An increase of soluble aluminum present in the cultures causes an increase of aluminum in both the roots and tops. Aluminum, being the third most abundant element, exists to some extent almost everywhere. In water cultures it enters as dust and as an impurity in the chemicals and water used; the solvent action of the nutrient solution on glass containers probably brings some into solution. This explains why the plants grown in the check cultures contained appreciable amounts of aluminum. Of significance is the fact borne out by the analyses that when plants are grown in cultures containing considerable aluminum, the iron content of the roots and tops is much less than if grown in cultures almost free of aluminum. It may be that iron is replaced in the plant to such an extent by aluminum that the plant cannot function properly.

TABLE 21

Fe_2O_3 and Al_2O_3 in rye tops grown in sand cultures with and without aluminum at various reactions

pH VALUE OF CULTURE	WITHOUT ALUMINUM		WITH ALUMINUM	
	Fe_2O_3	Al_2O_3	Fe_2O_3	Al_2O_3
	per cent	*per cent*	*per cent*	*per cent*
4.0	0.040	0.023	0.030	0.183
4.2	0.046	0.040	0.028	0.132
5.0	0.015	0.017	0.017	0.162
6.0	0.011	0.012	0.006	0.100
7.0	0.007	0.014	0.005	0.051
8.0	0.008	0.012	0.004	0.044
9.0	0.004	0.011	0.003	0.087

The data indicate that the barley contained a higher average percentage of aluminum than rye. The greater permeability of barley to aluminum may explain why barley is less tolerant to aluminum than rye.

Stoklasa (56) obtained somewhat similar results with *Pragmites communis*. He is of the opinion that when large amounts of aluminum or iron enter the plant there is an equivalent migration of other ions such as potassium. He also states that aluminum causes a coagulation of the proteins.

To obtain data on the effect of aluminum on root growth, the author performed the following experiment. Barley and rye were germinated in coarse, acid-digested silica sand. The seedlings were transferred to solution cultures with and without aluminum at the same acidities. These solutions were changed daily. After 3 days it was noticed that the roots of barley in the cultures containing aluminum were coarse and had few lateral rootlets. Barley at similar reactions in cultures without aluminum had a great number of lateral rootlets. With rye, 100 p.p.m. of alumina did not prevent the formation of lateral rootlets but markedly decreased the number formed.

Microscopical examinations revealed that the amount of aluminum present had little if any effect on the number of root hairs.

GENERAL DISCUSSION

Under well-aerated conditions it is very improbable that aluminum salts of organic acids exist in soils in appreciable amounts, due to rapid destruction of simple organic acids. The aluminum salts of sulfuric, nitric and hydrochloric acids are probably present in small amounts in acid soils, being probably formed by the action of these acids upon some rather easily soluble aluminum compound such as gibbsite. Soil biologists are skeptical as to whether aluminum can serve as a base for nitrification or that nitrification can go on at reactions acid enough to form considerable amounts of soluble aluminum compounds. Sulfofication, on the other hand, can go on at very acid reactions, and it is entirely possible that the acid so developed can bring aluminum into solution.

Salts of aluminum, such as aluminum sulfate, hydrolyze in solution with the liberation of an acid. On neutralization of the acid, aluminum hydroxide is precipitated. In fact, in the acid range, solubility determinations show that only in solutions more acid than pH 4.7 can quantities of aluminum greater than 3 p.p m. exist in solution. The presence of salts, such as calcium nitrate and magnesium sulfate, which do not react to form insoluble salts of aluminum, does not seem to have much influence on the solubility. Hence it is natural to suppose, and in fact it is true, that the solubility of aluminum in the soil solution at a given reaction is practically the same as in water at that reaction. Phosphates are usually not present in sufficient amount in the soil solution to affect appreciably the solubility of aluminum.

Aluminum forms with the alkalies soluble salts called "aluminates." Consequently, in alkali soils soluble aluminum may be present as sodium and potassium aluminates. Just as in acid solutions, the amount of soluble aluminum in an alkaline solution is dependent on the pH value. At pH 8.5 and above, considerable amounts of aluminum are found in solution.

In order to show more clearly and concisely the cases in which aluminum exerted a toxic action in the plant cultures, the ratio of plant growth with aluminum to that without aluminum was calculated. The weights used included both tops and roots. Thus a ratio approaching 1.0 shows that the plants grew as well in cultures with aluminum as without it. A ratio approaching zero means that the plants in the cultures containing aluminum produced a very low weight compared to those of the corresponding aluminum-free cultures. The data from these calculations are given in tables 22 and 23.

These data indicate that with all crops studied, aluminum exerts a pronounced toxic action when present in concentrations of 50 to 100 p.p.m. as was the case in the cultures at pH 4.2 and 4.0. Decidedly smaller amounts of aluminum, such as present in the other cultures, produced a far less toxicity.

The amount of soluble aluminum which plants can tolerate without having

their growth reduced in any way no doubt differs with the plant. An examination of Conner's data (17) indicates that he found little aluminum injury to barley at pH 5.0. Recalculation of his results shows that he added 12.2 p.p.m. Al_2O_3 to the culture. In all probability some of the aluminum was precipitated at this pH value and if the cultures were kept at pH 5.0, he probably had 2 to 3 p.p.m. remaining in solution. The writer obtained results indicating that barley was retarded some when grown in a nutrient solution saturated with aluminum at pH 5.0.

TABLE 22

Ratio of plant growth with aluminum to that without aluminum for alfalfa, barley and rye at reactions indicated

REACTION	RATIOS		
	Barley	Rye	Alfalfa
4.0	0.29	0.68	Dead*
4.2	0.39	0.53	Dead*
5.0	0.77	0.90	1.12
6.0	0.84	1.15	0.97
7.0	0.87	1.09	1.07
8.0	0.86	0.92	Omitted
9.0	0.90	0.95	Dead with Al*

* Alfalfa at pH 4.0 and 4.2 died both with and without aluminum. At pH 9.0 it died with aluminum, and barely lived without aluminum.

TABLE 23

Ratio of plant growth with aluminum to that without aluminum for corn, oats, soybeans and red clover at reactions indicated

REACTION	RATIOS			
	Corn	Oats	Soybeans	Red Clover
4.0	0.29	0.48	0.30	0.27
4.2	0.22	0.49	0.78	0.25
4.7	0.57	0.73	0.67	0.70
5.6	0.80	0.97	0.77	1.80
6.0	0.70	0.90	0.80	1.01
6.4	0.84	1.03	1.11	0.93

Alkaline soils have been found by the writer to contain soluble aluminum salts. The greenhouse experiments prove soluble aluminum to be toxic at alkaline reactions as well as acid ones. Only when the reaction approaches pH 8.5 to 9.0 or above does the soil solution contain considerable amounts of aluminum. Soils having reactions of this order are by no means rare in the United States and are probably far more abundant than soils of pH 4.4 or 4.2, a reaction at which approximately equivalent quantities of aluminum are present in acid soil solutions. For this reason severe aluminum toxicity is probably more frequent in alkaline soils than in acid ones.

SUMMARY

This investigation was undertaken to ascertain whether the decreased growth of some plants on acid soils can be attributed to the toxic effect of soluble aluminum, wholly or in part, rather than to an excessive hydrogen-ion concentration.

The solubility of aluminum compounds in water, nutrient solutions and soil solutions at various reactions was determined. Later, greenhouse tests were made, barley, rye, alfalfa, red clover, corn, oats, and soybeans being grown in two series of quartz sand cultures at various reactions, supplied with a nutrient solution which in one series was saturated with aluminum. The growth in this series was compared with the otherwise identical series to which no aluminum had been added and the toxic effect of aluminum thus ascertained.

In this work, aluminum, except when present in very large amounts, was determined by precipitation as the phosphate, precipitation being made at about pH 5.0. The precipitate was ignited, weighed, and corrected for the weight of iron phosphate present. Studies made by the writer have shown that at pH 5.0, aluminum as phosphate is completely precipitated whereas calcium remains in solution.

The curve for the solubility of aluminum in the soil solution at various reactions practically coincides with the curve for the solubility of aluminum in water at the same reactions. In fact, soil solutions obtained from natural and artificially produced acid and alkaline soils contained quantities of aluminum which could have been predicted quite closely by a knowledge of their pH value and reference to the curve showing solubility of aluminum in water at various reactions. Dialysis of soil solutions from acid and alkaline soils through collodion bags showed that the aluminum was present in true solution.

The data relating to the solubility of aluminum in water and soil solutions show that at pH 5, there is 1 to 2 p.p.m. of Al_2O_3 in solution. As the acidity decreases to the neutral point the solubility decreases to almost nothing. When the acidity becomes greater than pH 5 the solubility increases rather rapidly until pH 4.5 is reached at which point the solubility increases very rapidly. When the relation of plant growth to these acidities and solubilities is considered, it is found as follows:

At very strong acidities, that is, acidities greater than pH 5.0, all the crops except alfalfa suffered both strong aluminum toxicity and strong H-ion toxicity. At these strong acidities, the alfalfa died whether aluminum was added or not.

At acidities less than pH 5.0 or thereabouts, alfalfa, red clover, rye and oats suffered little or no aluminum toxicity, while the corn, barley and soybeans suffered appreciably. At these same last named acidities, as regards H-ion toxicity, alfalfa and red clover suffered greatly; barley, corn, oats and rye suffered much less but still appreciably; and soybeans suffered little or not at all.

Since most of the acid soils found under field conditions fall within the range pH 5 to 7, it follows from the data presented that the benefit arising in practice through the use of lime in the case of clover, alfalfa, oats and rye results usually from a decrease in acidity and not

from a decrease of soluble aluminum present. In the case of corn and barley over the same range of acidity, this benefit results from a decrease both in acidity and in soluble aluminum. In the case of soybeans the benefit is due more, apparently, to a decrease in soluble aluminum. In the case of soils more acid than pH 5.0 the benefit of liming to all crops studied appears to come almost equally from a decrease in acidity and soluble aluminum present.

Strongly alkaline soils were found by the writer to contain large amounts of soluble aluminum. Thus one soil solution having a pH value of 9.01 contained 31 p.p.m. of aluminum oxide. The presence of soluble aluminum in strongly alkaline soils coupled with the toxicity of aluminum to plants in alkaline solutions suggests that one of the reasons why very alkaline soils do not support good plant growth is because of the soluble aluminum present.

Plants grown in sand cultures with and without soluble aluminum were analyzed for aluminum and iron. When grown in cultures to which aluminum had been added, the percentage of aluminum in the plant increased while that of iron decreased, indicating a possibility that aluminum was displacing iron.

Aluminum in water cultures was found to prevent the formation of lateral rootlets on barley but not on rye. In the case of rye, however, the lateral root development was restricted by aluminum.

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PLATE 1

FIG. 1. Barley grown in sand cultures of different reactions without aluminum. The numbers give approximate pH values of the cultures.

FIG. 2. Barley grown in sand cultures of different reactions with aluminum. The numbers give approximate pH values of the cultures.

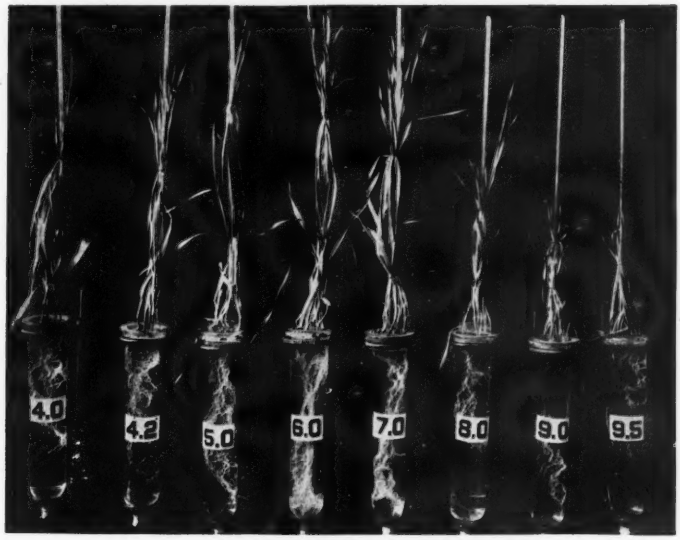

FIG. 1

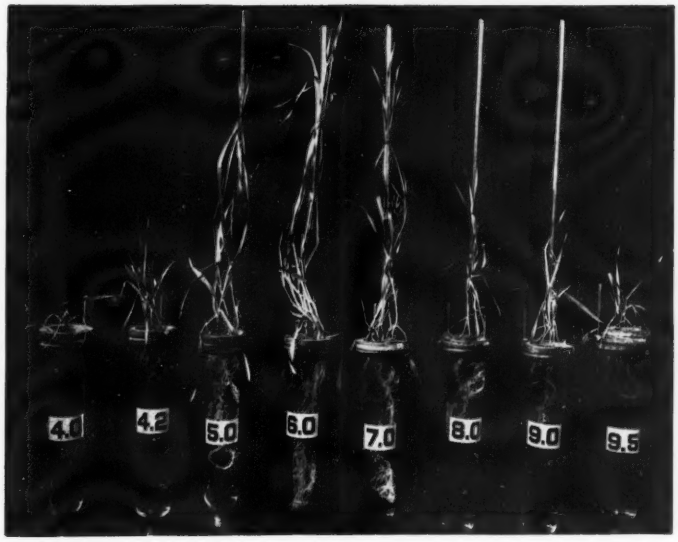

FIG. 2

PLATE 2

FIG. 1. Rye grown in sand cultures of different reactions without aluminum. The numbers give approximate pH values of the cultures.

FIG. 2. Rye grown in sand cultures of different reactions with aluminum. The numbers give the approximate pH values of the cultures.

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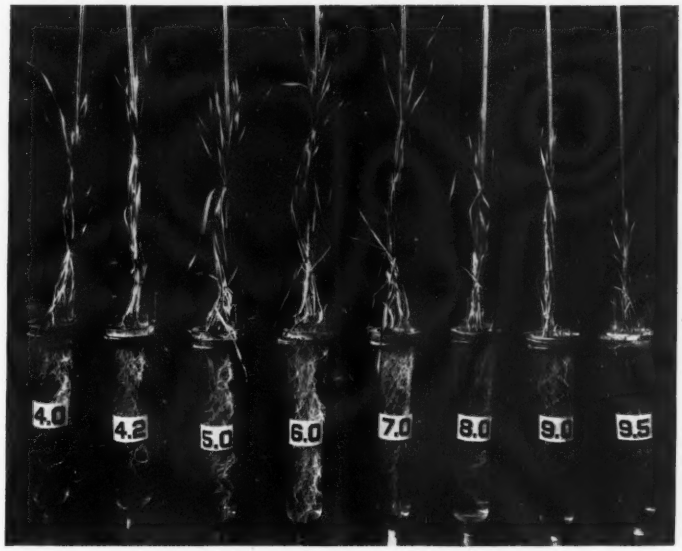

FIG. 1

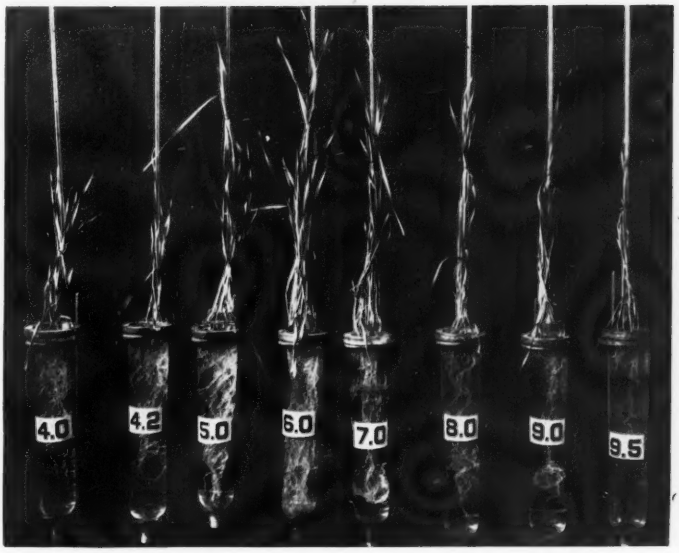

FIG. 2

PLATE 3

FIG. 1. Oats grown in sand cultures of different reactions without aluminum. The numbers give approximate pH values of the cultures.

FIG. 2. Oats grown in sand cultures of different reactions with aluminum. The numbers give approximate pH values of the cultures.

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FIG. 1

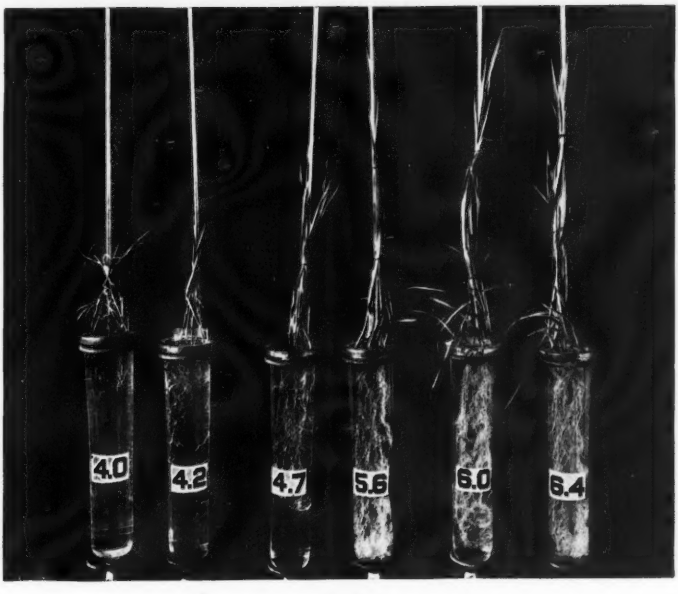

FIG. 2

PLATE 4

FIG. 1. Soybeans grown in sand cultures of different reactions without aluminum. The numbers give approximate pH values of the cultures.

FIG. 2. Soybeans grown in sand cultures of different reactions with aluminum. The numbers give approximate pH values of the cultures.

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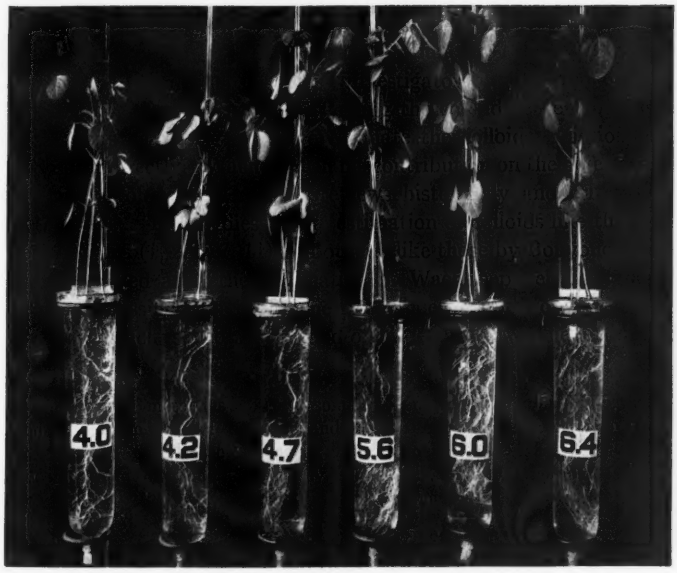

FIG. 1

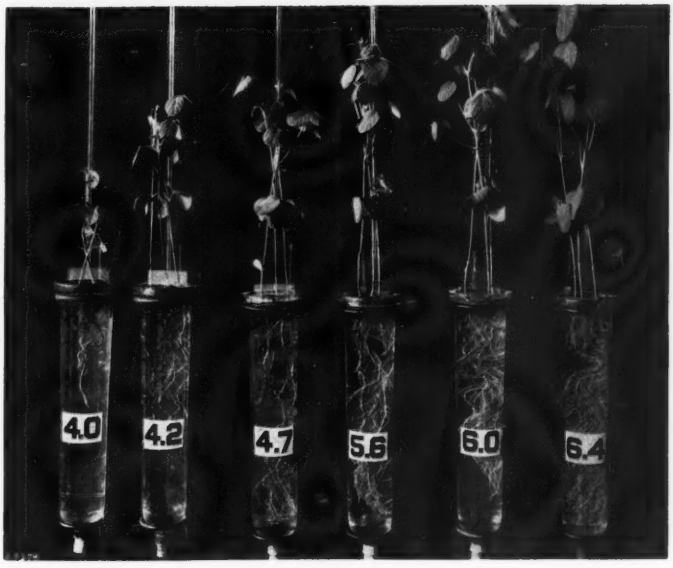

FIG. 2

PLATE 5

FIG. 1. Corn grown in sand cultures of different reactions without aluminum. The numbers give approximate pH values of the cultures.

FIG. 2. Corn grown in sand cultures of different reactions with aluminum. The numbers give approximate pH values of the cultures.

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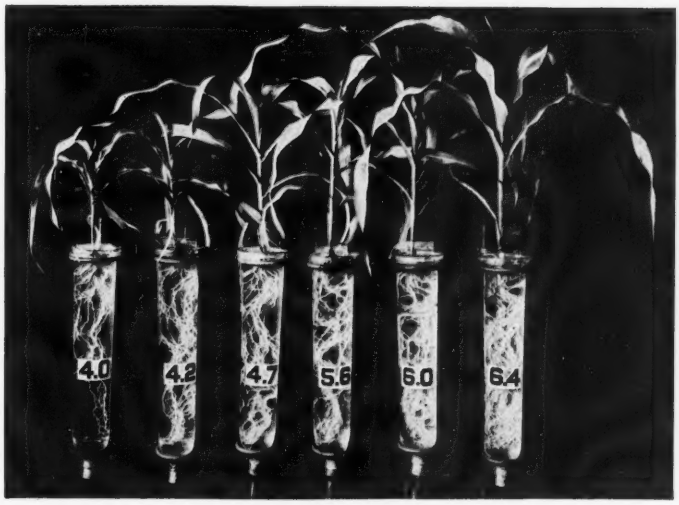

FIG. 1

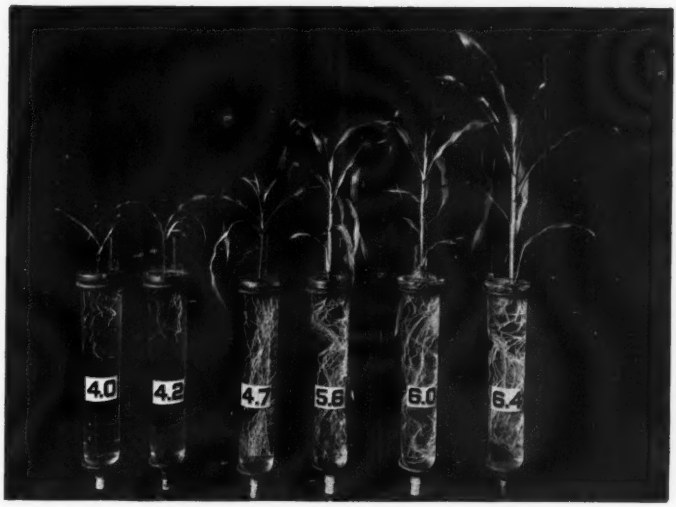

FIG. 2

PLATE 6

FIG. 1. Red clover grown in sand cultures of different reactions without aluminum. The numbers give approximate pH values of the cultures.

FIG. 2. Red clover grown in sand cultures of different reactions with aluminum. The numbers give approximate pH values of the cultures.

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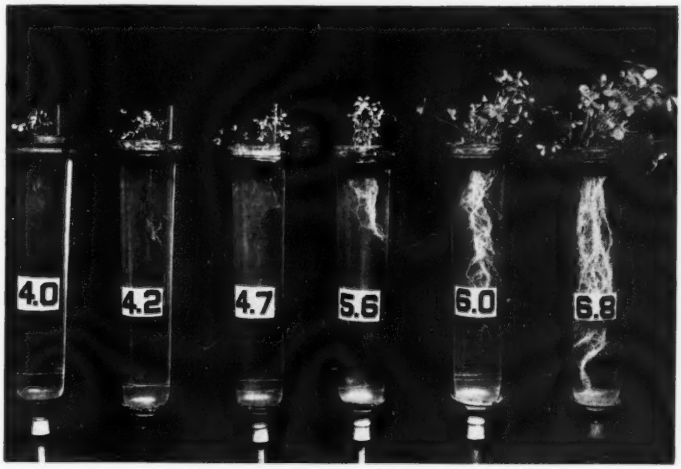

FIG. 1

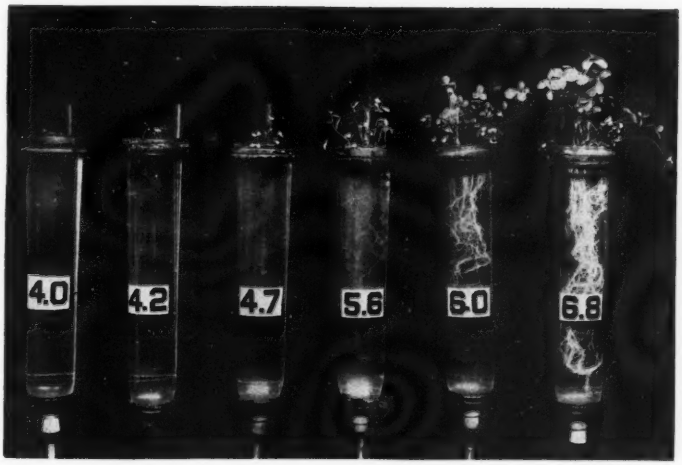

FIG. 2

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THE COMPARATIVE GROWTH OF PINEAPPLE PLANTS WITH AMMONIA AND NITRATE NITROGEN

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INTRODUCTION

It has long been known that many agricultural plants are able to utilize ammonia nitrogen directly, without waiting for nitrification to take place. An excellent review of the early investigations upon this problem is given by Hutchinson and Miller (2). These two workers carried out a carefully controlled series of experiments with wheat and peas. The seeds were sterilized in antiseptic solutions, and were germinated under aseptic conditions. The small plants were later transferred to sterile nutrient solutions containing nitrogen derived from either sodium nitrate or amonium sulfate. It was concluded that agricultural plants of various kinds can produce normal growth when supplied with nitrogen in the form of ammonium salts under conditions which exclude the possibility of nitrification.

Pantanelli and Severini (6, 7) worked with wheat, rice, corn and flax, which they grew in nutrient solutions supplied with a variety of ammonium salts, under conditions which precluded nitrification. They believed that ammonium salts have a higher coefficient of utilization than nitrate salts, if both ions of the ammonium compound can be utilized by the plant at approximately the same rate.

Prianishnikov (8) has reported a number of studies in which *Vicia sativa* and *Zea mays* were grown in nutrient solutions containing ammonium chloride and calcium carbonate. These plants were contrasted with those grown in complete nutrients where nitrogen was furnished by calcium nitrate. By renewing twice each week the solutions containing ammonium salts, the plants made five to six times the growth obtained without such a renewal. It was concluded that plants absorb ammonia nitrogen energetically as long as the reaction of the medium does not hinder the immediate transformation of the nitrogen into organic nitrogen combinations.

Similar successful results have been reported by Shulov (9) where he grew maize in sterile cultures containing nitrogen furnished by ammonium sulfate. Jones and Shive (3, 4) have recently grown wheat plants in nutrient solutions where the nitrogen was supplied by ammonium sulfate. These cultures were contrasted with a series where nitrogen was derived from potassium and calcium nitrates. The solutions with ammonia nitrogen became more acid; those

with nitrate nitrogen grew less acid in reaction. This change in reaction was found to be especially significant in altering the availability of the iron phosphate which furnished iron to part of the cultures.

McGeorge (5) has experimented with sugar cane in sand and water cultures in which he supplied nitrogen in the ammoniacal form and contrasted these cultures with a series where only nitrate nitrogen was present. He obtained an excellent growth of both tops and roots in the nitrate cultures. The cane in the ammoniacal solutions sent out strong, vigorous shoots but practically no root development took place, and after a few weeks the shoots withered and died. McGeorge concluded that sugar cane cannot grow without some nitrate nitrogen.

In the Hawaiian Islands fertilizer experiments have been carried out which have contrasted sodium nitrate, ammonium sulfate and dried blood as sources of nitrogen for pineapple culture. Some deleterious effects have generally been noted from sodium nitrate, although organic nitrogen and ammonia nitrogen have given uniformly good results. As a consequence of this work, only organic materials and ammonium sulfate are used as sources of nitrogen in the mixed fertilizers applied to pineapples.

It was desirable to know, therefore, whether the pineapple plant could use ammonia nitrogen directly or whether the ammonia salts had to undergo nitrification before they were available to the plant. As the pineapple plant makes an excellent growth in nutrient solutions, the following experiment was carried out in water cultures.

METHODS OF EXPERIMENTATION AND SOLUTIONS EMPLOYED

Three types of planting material are used for the propagation of pineapple plants: first, slips, which are the shoots attached to the sides of the stem of the pineapple fruit; second, suckers, which are the shoots arising from buds in the axils of the leaves; third, crowns, which are obtained from the tops of the fruits. In field practice slips and suckers are preferred, as larger and more vigorous plants are obtained which fruit earlier than plants grown from crowns. As there is more individual variation, however, in plants grown from slips and suckers, crowns have been employed in the cultural experiments.

Before starting the crowns in the nutrient solutions, the smaller basal leaves were removed and the crowns were cured upside down in the open air and sun for several days. This is similar to the treatment given in field practice and helps to prevent mildew and rotting of the tissue, before the roots begin to develop.

The solutions used were the same as those employed by McGeorge in his work with sugar cane. The nitrate solution was essentially the same solution used by Hoagland (1). The plants were grown in 4-gallon glazed stoneware crocks, with special covers of the same material. These covers had a round hole in the center, which permitted the base of the crowns to reach just to the solution. In each of the normal nutrient solutions 6 duplicate plants were

TABLE 1

Composition of nutrient solutions

	RE-ACTION	POTASSIUM (K)	CALCIUM (Ca)	MAGNESIUM (Mg)	PHOSPHATE (PO_4)	NITROGEN (N)	SULFATE (SO_4)
	pH	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
Nitrate solution, normal nutrient	6.6	190.0	172.0	52.0	117.0	160.0	202.0
Nitrate solutions, diluted 1:4	6.6	47.5	43.0	13.0	29.2	40.0	50.5
Ammonia solution, normal nutrient	6.8	190.0	172.0	52.0	117.0	160.0	202.0
Ammonia solution, diluted 1:4	6.8	47.5	43.0	13.0	29.2	40.0	50.5

TABLE 2

Change in reaction of culture solutions for each period of growth

	INITIAL REACTION	AUGUST 14 TO OCTOBER 8	OCTOBER 8 TO NOVEMBER 3	NOVEMBER 3 TO DECEMBER 6	DECEMBER 6 TO JANUARY 7	JANUARY 7 TO FEBRUARY 12	FEBRUARY 12 TO MARCH 4	MARCH 4 TO APRIL 7
	pH	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*
Nitrate solution, normal nutrient	6.6	8.18	4.13	5.0	6.24	6.07	5.56	6.32†
	6.6	8.27	4.46	5.0	6.15	6.07	5.82	
	6.6	8.22	4.29	4.6	5.82	5.90	5.73	
	6.6	8.22	4.04	4.6	6.15	5.99	5.78	
	6.6	8.22	4.46	4.6	6.15	5.99	5.48	
	6.6	7.84	3.79	5.0	6.49	6.24	5.90	
Nitrate solution, 1:4 dilution	6.6	9.20	4.04	4.50	6.15	6.83	6.91	7.25†
	6.6	9.20	4.29	4.20	6.24	6.15	6.83	
	6.6	8.18	4.13	4.60	6.49	5.22	7.13	
	6.6	8.61	4.21	4.60	6.07	6.49	6.97	
	6.6	7.84	6.07	4.60	6.58	6.83	6.91	
	6.6	8.52	4.13	4.60	6.41	5.31	6.91	
Ammonia solution, normal nutrient	6.8	2.60	3.70	4.00	6.15*	6.49	5.90	3.95†
	6.8	2.60	3.70	3.80	6.24*	6.66	6.07	
	6.8	2.60	3.62	3.60	6.15*	6.66	5.14	
	6.8	2.60	3.62	3.80	6.07*	6.49	5.82	
	6.8	2.60	3.53	3.80	5.90*	6.47	6.07	
	6.8	2.70	3.62	3.90	5.82*	6.32	6.15	
Ammonia solution, 1:4 dilution	6.8	3.08	2.94	3.60	3.45*	3.79	3.22	3.53†
	6.8	3.08	3.02	3.40	3.62*	3.79	3.62	
	6.8	3.08	3.11	3.80	3.86*	5.05	3.88	
	6.8	3.08	3.11	3.40	3.86*	5.73	4.29	
	6.8	3.08	3.28	3.60	3.86*	4.63	3.70	
	6.8	3.08	3.11	3.80	3.97*	6.20	4.97	

* The ammonia cultures from this date received their calcium as calcium carbonate.
† Average of composite.

TABLE 3

Growth of pineapple plants in nitrate and ammonia cultures

Period 41 weeks from June 21, 1923 to April 7, 1924

TREATMENT	NUMBER OF PLANTS	WEIGHT OF CROWNS AT START	HARVESTING RESULTS, FRESH WEIGHTS					
			Weight of leaves and stem	Weight of roots	Length of roots	Total fresh weight of plants	Total gain in weight	Total dry weight of plants
		gm.	*gm.*	*gm.*	*cm.*	*gm.*	*gm.*	*gm.*
Nitrate solution, normal nutrient	31	98	1,024	55	76.2	1,079	981	116.0
	32	102	779	29	76.2	808	706	87.5
	33	92	753	38	94.0	791	699	81.0
	34	104	1,020	42	61.0	1,062	958	115.5
	35	124	1,040	44	71.0	1,084	960	110.0
	36	120	1,032	39	68.6	1,071	951	115.0
Mean						983.0±36.0	876.0±34.0	104.0±4.0
Standard deviation						130.0±25.0	123.0±24.0	14.4±2.8
Coefficient of variability						13.2± 2.6	14.0± 2.8	13.8±2.7
Nitrate solution, 1:4 dilution	37*	92	428	7	55.9	453	361	56.0
	38*	85	282	44	39.4	289	204	41.0
	39	107	685	50	76.2	729	622	88.0
	40	117	673	14	61.0	723	606	85.0
	41*	112	474	11	40.6	488	376	60.0
	42*	95	247	7	38.1	258	163	29.0
Mean						490.0±51.0	389.0±49.0	59.8±6.0
Standard deviation						186.0±36.0	179.0±35.0	21.4±4.2
Coefficient of variability						38.0±8.4	46.0±10.6	35.8±7.8

Ammonia solution, normal nutrient	43*	110	212	7	31.8	219	109	34.3
	44	105	275	10	27.9	285	180	35.0
	45	122	472	20	41.9	492	370	49.0
	46	82	332	15	36.8	347	265	36.0
	47	95	332	17	38.1	349	254	38.0
	48	92	322	15	31.8	337	245	37.0
Mean of nos. 44, 45, 46, 47 and 48						362.0±21.0	263.0±19.0	39.0±1.5
Standard deviation						69.0±15.0	62.0±13.0	5.0±1.1
Coefficient of variability						19.1± 4.2	23.6± 5.3	12.8±2.8
Ammonia solution, 1:4 dilution	49	85	487	30	50.8	517	432	56.0
	50	117	563	34	55.9	563	480	64.0
	51	105	492	25	57.1	517	412	52.0
	52	112	359	19	50.8	378	266	43.0
	53	100	515	30	43.2	545	445	57.0
	54	88	455	27	40.6	482	394	51.0
Mean						500.0±17.0	405.0±19.0	54.0±1.7
Standard deviation						61.0±12.0	68.0±13.0	6.0±1.2
Coefficient of variability						12.2± 2.4	16.8± 3.3	11.1±2.2

* These plants showed clear evidence of pineapple wilt.

grown and another set of 6 was grown in each of the normal nutrient solutions diluted 1:4. Table 1 gives the composition of the nutrient solutions.

The salts used in making the nitrate solution consisted of potassium nitrate, calcium nitrate, sodium nitrate, monobasic potassium phosphate, and magnesium sulfate. The salts used in making the ammonia nutrient solution were ammonium chloride, magnesium sulfate, monobasic potassium phosphate, potassium sulfate and calcium sulfate. Later in the experiment calcium carbonate was substituted for calcium sulfate in the ammonium solutions. Each of the 4-gallon crocks received 12.5 liters of nutrient solution. Each 4-gallon culture jar also received 4 cc. of a solution of iron citrate which contained 0.0022 gm. iron (Fe) per cubic centimeter, or a total of 0.008 gm. iron. The solutions were changed at intervals of approximately one month, though the reaction was tested frequently to note the rapidity of change in the two sets of cultures. The periodic determinations of reaction were made colorimetrically with Clarke and Lub's buffer solutions and group of selected indicators. The final determinations were made electrometrically.

The first group of ammonia cultures was made up with sterile solutions and water, but it was not possible to attempt any sterilization of the pineapple crowns. The solutions were tested for freedom of nitrates at frequent intervals. No nitrates were ever found in the ammonia cultures. It is, of course, possible that small amounts of nitrates might have been formed and immediately absorbed by the plant. Some sets of the series of solutions were analyzed after the plants had grown in them and these solutions were on several occasions allowed to stand for a sufficient interval to permit nitrification to take place had the cultures been contaminated. There is strong evidence that no nitrification took place in the ammonia cultures, for in each case they were found free from nitrates.

The changes in reaction of each set of cultures are given in table 2. It will be noted that the experiment started on August 14, 1923 and the plants were grown until April 7, 1924. The reaction given for each period is the final determination made just before the solutions were changed. The plants were allowed to grow in the first set of solutions for more than the month's period which was later adopted.

In the first period of growth both groups of nitrate cultures showed an appreciable change in reaction, toward alkalinity. During the later progress of the experiment there was a constant tendency for the nitrate solutions to become more acid in reaction.

The ammonia cultures steadily increased in acidity at all periods of the experiment. The change in reaction took place so rapidly, that it was decided to substitute calcium carbonate for calcium sulfate in making up the ammonia nutrient solutions. The required amount of the precipitated calcium carbonate was added to each culture jar after the final dilution was made. This delayed the rapid change in reaction which formerly occurred.

GROWTH OF PLANTS IN NITRATE AND AMMONIA CULTURES

The summarized results of the increase in weight of the pineapple plants in the different groups of solutions are given in table 3. The arithmetical mean weight of each group has been calculated on both the fresh weight and on the dry basis. The mean gain of the plants over the weight of the respective crowns has also been determined. The standard deviation has been found by the usual statistical method by squaring the deviation of the weight of each plant from the mean, taking the sum of the squares thus found, dividing this figure by the total number of determinations made and taking the square root of the quotient. The percentage ratio of the standard deviation to the mean gives the coefficient of variability which shows the percentage deviation on

TABLE 4

Change in composition of nutrient solutions

	POTASSIUM (K)	CALCIUM (Ca)	MAGNESIUM (Mg)	PHOSPHATE (PO_4)	AMMONIA NITROGEN (N)	NITRATE NITROGEN (N)	REACTION
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*pH*
Original nutrient solutions							
Normal nutrient	190.0	172.0	52.0	117.0	160.0 or	160.0	6.6–6.8
Nutrient, 1:4 dilution	47.5	43.0	13.0	29.2	40.0 or	40.0	6.6–6.8
Solutions of January 7 to February 12							
Nitrate, normal nutrient	26.0	55.2	48.6	75.5	....	68.8	6.74
Nitrate, 1:4 dilution	14.4	14.4	9.6	13.6	....	16.0	7.84
Ammonia, normal nutrient	150.5	40.8	43.6	92.5	98.7	....	5.81
Ammonia, 1:4 dilution	9.5	25.2	11.2	8.9	11.7	....	3.45
Solutions of March 4 to April 7							
Nitrate, normal nutrient	16.5	54.8	39.4	77.2	....	67.2	6.32
Nitrate, 1:4 dilution	20.5	16.8	12.8	18.3	....	23.2	7.25
Ammonia, normal nutrient	136.5	19.6	9.3	88.3	117.6	....	3.95
Ammonia, 1:4 dilution	11.0	14.8	10.6	9.3	23.1	....	3.53

either side of the mean, within which range approximately two-thirds of the plant weights will be found.

From an examination of these figures it may be seen that the mean figures show significant differences in weight between the plants grown in the normal nitrate solution and any of the other groups. These plants have unquestionably made the best growth. The next best growth was made by the series grown in the dilute ammonia solutions. This series might have been excelled by the plants grown in the dilute nitrate solutions, but 4 of the 6 plants in this series had partly failed with typical pineapple wilt before the close of the experiment. The partial failure of the 4 plants in the dilute nitrate series is reflected in the high degree of variability shown in the weights of these plants.

TABLE 5

Composition of green pineapple plants grown in nitrate and ammonia cultures

CULTURE SOLUTION	DETERMINED IN ORIGINAL MATERIAL			ASH CONSTITUENTS CALCULATED TO ORIGINAL PLANTS											
	Moisture	Nitrogen (N)	Ash	Silica (SiO_2)	Lime (CaO)	Magnesia (MgO)	Manganese (Mn_3O_4)	Potash (K_2O)	Soda (Na_2O)	Phosphate (P_2O_5)	Iron (Fe_2O_3)	Alumina (Al_2O_3)	Chlorine (Cl)	Sulfates (SO_4)	Carbon dioxide (CO_2)
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Nitrate normal nutrient	89.16	0.22	1.36												
	89.35	0.22	1.45												
	89.78	0.22	1.39	0.011	0.081	0.060	0.005	0.701	0.109	0.085	0.011	0.006	0.054	0.092	0.257
	89.12	0.23	1.45												
	89.81	0.21	1.37												
	89.25	0.23	1.44												
Mean	89.41	0.22	1.41												
Nitrate 1:4 dilution	87.39*	0.20	1.19	0.025	0.096	0.127	0.005	0.704	0.155	0.121	0.046	0.014	0.187	0.127	0.193
	85.82*	0.26	1.60												
	87.88	0.18	1.10												
	88.26	0.19	1.17	0.017	0.079	0.069	0.006	0.532	0.111	0.103	0.021	0.012	0.078	0.110	0.157
	87.76	0.21	1.21												
	88.66	0.22	1.43												
Mean	87.63	0.21	1.28												
Ammonia normal nutrient	83.96*	0.42	1.97	0 020	0.081	0.084	0.009	0.800	0.254	0.301	0.095	0.026	0.404	0.149	0.005
	87.64	0.32	1.49												
	90.04	0.23	1.29												
	89.46	0.28	1.31	0.010	0.042	0.055	0.004	0.570	0.101	0.198	0.033	0.022	0.286	0.085	0.002
	89.16	0.29	1.41												
	88.82	0.30	1.26												
Mean	88.18	0.31	1.45												

Ammonia 1:4 dilution	89.33	0.27	0.98	0.018	0.044	0.050	0.004	0.531	0.094	0.153	0.021	0.014	0.226	0.078	0.018
	89.17	0.27	1.08												
	89.84	0.25	1.19												
	88.58	0.28	1.45												
	89.32	0.27	1.16												
	89.45	0.26	1.20												
Mean	89.28	0.27	1.17												

* These plants failed with typical wilt.

The poorest growth was made by the plants grown in the normal ammonia nutrient solutions. One of these plants began to fail from wilt but its weight has been excluded from the figures used in the calculation of the mean.

The comparative growth of plants and roots is clearly shown in plates 1 and 2. The root growth of the plants grown in the normal ammonia nutrient was greatly restricted, both in total length and in the development of root hairs.

CHANGE IN COMPOSITION OF NUTRIENT SOLUTIONS

In order to obtain some information as to the abstraction of nutrients from the culture solution, the solutions removed from the culture jars on February 7 and January 12 were analyzed. The results are given in table 4. With the better growing plants in both the nitrate and ammonia cultures the largest proportionate abstraction of a nutrient was the amount of potassium removed. Next after this was lime, nitrogen and phosphate. In general the smallest demand at this period was made upon the magnesium. The percentage of the total nutrient present absorbed by the plants corresponds to the relative growth made by the various series. In other words the plants growing in the normal nitrate nutrient took up the largest proportion. This was followed by the dilute ammonia series and the dilute nitrate series. The lowest absorption was made by the normal ammonia series. There was no consistent difference in the relation of the ions absorbed by the two nitrate series compared to the plants receiving nitrogen in the ammoniacal form.

COMPOSITION OF THE PLANTS

The analyses made upon the plants grown in this experiment are given in table 5. The percentages of moisture, nitrogen and ash were determined in the individual plants grown in each series. The composition of the ash of composite samples from each group of normal plants was determined. Separate analyses were also made of the ash of the plants which failed with wilt in the dilute nitrate and normal ammonia nutrient. These ash constituents were all calculated back to the average moisture content of the green plants in the series.

The plants in all the series showed the large absorption of potash which was indicated by the analysis of the culture solutions. The other nutrients were present in somewhat the same proportions indicated by the determinations upon the solutions, except that magnesium was taken evidently in larger amounts during the earlier part of the plant's growth.

Almost the only constituent which was absorbed in notably different proportions by the two nitrate series compared to the ammonia series is lime. The nitrate series contained approximately twice as high a content of lime as did the ammonia series, though the one plant in the normal ammonia series which failed from wilt contained a higher content of lime than the others in this

group. It might also be noted that the plants in the nitrate series all showed a notably higher content of carbon dioxide in the ash.

Beyond these slight differences no notable differences can be observed in the composition of the various series.

CONCLUSIONS

The results of the above work appear to demonstrate that the pineapple plant is capable of assimilating all its nitrogen in the form of ammonia salts.

The best growth, however, was made by plants growing in the normal nitrate nitrogen cultures. The plants growing in nitrate cultures of one-fourth this dilution made a poor growth and showed clear evidence of a tendency to fail with typical pineapple wilt.

Under the conditions of this experiment the ammonia nitrogen was not readily utlized from the full strength normal nutrient solutions. The plants in the ammonia cultures diluted one-fourth made a better development than those in the full strength solutions.

This would appear to suggest that under field conditions the pineapple plant probably uses nitrogen in both the nitrate and ammoniacal forms.

The nitrate cultures changed to a more alkaline reaction during the early period of their growth. Later in their development these cultures developed a distinctly more acid reaction than the initial pH of the solutions.

The ammonia cultures at all times made a rapid change toward a more acid reaction of the nutrient solutions.

The analysis of the nutrient solutions in which plants had grown during the latter part of the experiment showed that the potash was absorbed in largest amount from the solutions. The next greatest demand was for nitrogen. The absorption from the various series of culture solutions corresponded to the growth made by the plants.

The analysis of the plants confirmed the fact that potash was stored in largest amounts, and next in order was nitrogen. The only notable difference in the composition of the plants grown in the nitrate and ammonia cultures was a low content of lime in the ammonia plants. The ash of the ammonia plants was also low in its percentage of carbon dioxide.

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PLATE 1

Fig. 1. Root development of pineapples grown in normal nitrate nutrient.

Fig. 2. Root development of pineapples grown in normal ammonia nutrient.

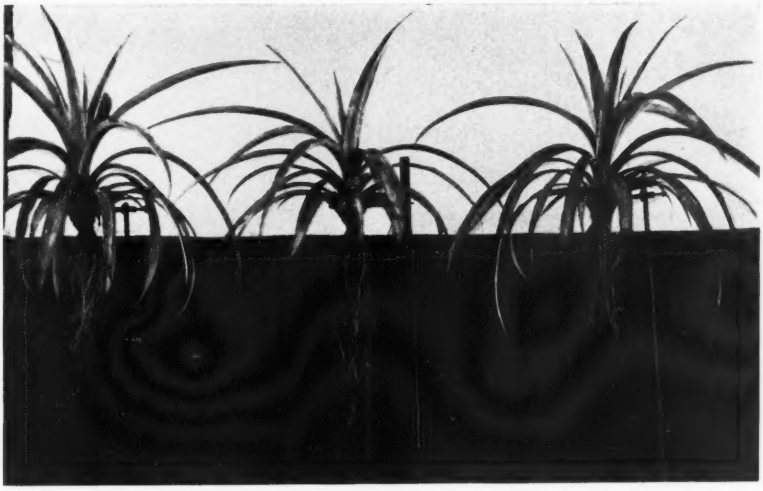

FIG. 1

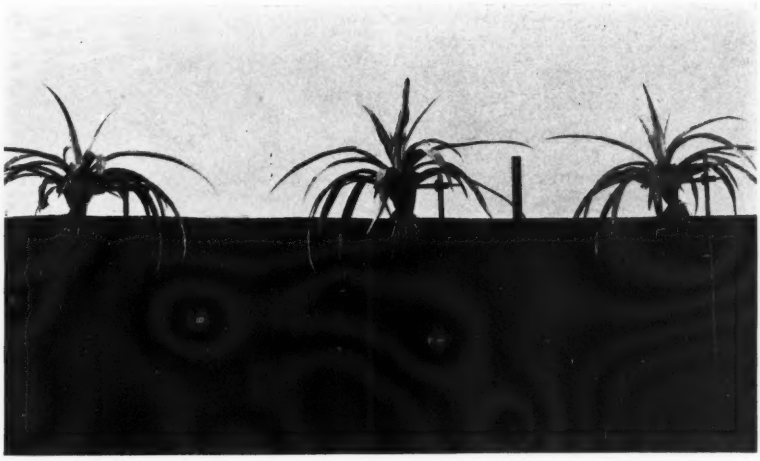

FIG. 2

PLATE 2

FIG. 1. Comparison of jars 32, 34, 36, normal nutrient, nitrogen as nitrate, contrasted with 37, 40, 41, nitrate nutrient, 1:4 dilution.

FIG. 2. Comparison of jars 44, 46, 48, normal nutrient, nitrogen as ammonia, contrasted with 50, 52, 54, ammonia cultures, 1:4 dilution.

FIG. 3. Comparison of jars 44, 46, 48, normal nutrient, nitrogen as ammonia, contrasted with 32, 34, 35, normal nutrient, nitrogen as nitrate.

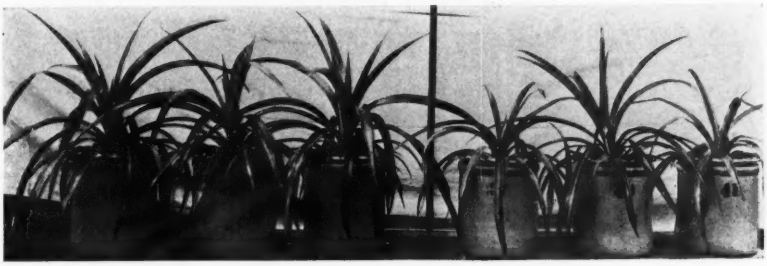

FIG. 1

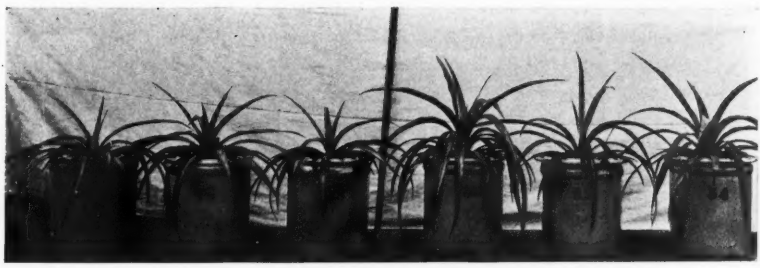

FIG. 2

FIG. 3

UNIV. OF MICH.

SOME MOISTURE RELATIONSHIPS OF SOILS

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It was brought out in an early contribution (4) that as the water content of the soil decreases in an arithmetic progression, the freezing point depression increases in a geometric progression. As an explanation of this, the hypothesis was offered that some of the water contained by the soil is either loosely chemically combined or physically adsorbed, or both, in which event this portion of the water is not free to act as a solvent but is removed from the liquid phase and takes no part in the lowering of the freezing point. By means of the dilatometer method (1) it was shown that some of the water present in the soil will not freeze, the amount varying with such factors as the class of the soil and the degree of supercooling. On the basis of these results (2) the moisture in the soil was classified into gravitational, free and unfree, the unfree water being made up of capillary, adsorbed and combined. The latter may be in part water of hydration and in part water of solid solution. In a still later report (3) additional information on the forms of water that exist in the soil, their movements and plant relationships was presented.

More knowledge was obtained while studying the adsorptive capacity for potassium of several muck soils when brought into contact with a normal solution of potassium chloride. In making these studies 5 gm. of the dry materials was shaken with 60 cc. at frequent intervals for approximately 16 hours. The mass was filtered, an aliquot portion of the filtrate taken and the content of potassium determined in the usual manner. There was found to be a greater concentration of potassium present in the filtrates than in the original salt solution. The soils used, together with certain of their properties and data obtained, are shown in table 1.

The increase in the amount of potassium in the filtrate over the original salt solution may be due to some of the water becoming inactive. If a given amount of soil takes up or makes unfree 5 cc. of water from a salt solution and is capable of removing only as much of the base as is contained in 1 cc. then the concentration of the salt solution becomes stronger. The water so fixed, seems not to function as a solvent, otherwise there would be a decrease in the amount of potassium in solution, since the soil would take some of it out of the solution.

McCall, Hildebrandt and Johnston also obtained similar results (5). They use the term "negative adsorption" to explain the phenomenon.

Additional studies on this problem were conducted with sucrose. This substance was used because it does not react with the soil as do mineral salts, and if the soil removes water from it, the freezing point depression should become greater. In these investigations the increases in concentration of the molar sucrose solution when brought into contact with different soils and soil separates were measured by means of the freezing point method. Soils dried at each temperature were weighed in duplicate in freezing tubes, and

TABLE 1

Increase in K in KCl when added to organic soils

SAMPLE NUMBER	COLOR	TEXTURE	INCREASE IN K*
			mgm.
1	Brown	Coarse	141.0
3	Brown	Coarse	79.9
5	Dark brown	Finely divided	133.0
15	Dark brown	Coarse	43.6
17	Black	Finely divided	56.5
18	Dark brown	Finely divided	69.3

* Increase in concentration of K in filtrate over original solution of KCl, 60 cc. *N* KCl added to 5 gm. of soil.

TABLE 2

Water removed from sucrose solution by organic soils, and probably made unfree or inactive

NUMBER OF SAMPLE	TEMPERATURE		
	100°C.	55°C.	Room temperature
	per cent	*per cent*	*per cent*
2	26.10	.....	16.90
4	33.65	27.02	18.30
5	29.03	29.70	18.97
6	31.22	28.91	19.39
7	34.75	24.75	18.13
8	35.84	29.95	20.13
10	34.75	23.64	16.70
11	30.86	28.80	20.00
14	33.46	25.46	19.40
15	28.82	27.95	20.29

securely stoppered with rubber stoppers. Those that had to be oven-dried were dried before being stoppered, and their dry weight was determined. In making the freezing point determinations 10 cc. of distilled water was added to one tube, and to its duplicate was added sucrose solution from a pipette calibrated to deliver solution enough to contain 10 cc. of water.

The sugar solution was added immediately on unstoppering the tubes, to prevent absorption of moisture from the air. The freezing point determinations were made on the two samples and the percentages of unfree water were

calculated. The method of calculating may be explained by the use of the following formula:

$$\frac{100\left(\text{cc. } H_2O \text{ used} - \frac{\text{cc. } H_2O \text{ used} \times \text{F. P. of sucrose solution}}{\text{F. P. of mixture} - \text{F. P. of soil and } H_2O}\right)}{\text{gm. of oven-dry soil}} = \text{per cent unfree } H_2O$$

TABLE 3

Water removed from sucrose solution by different mineral soil horizons and probably made unfree or inactive. Dried at 100°C.

SOIL TYPE	HORIZON	WATER REMOVED
		per cent
Ontonagon	A_1	2.5
	A_2	2.6
	B	3.5
Ontonagon colloids	B	6.5
	C	2.3
Miami	A_1	2.7
	A_2	1.9
	B	2.1
	C	2.4
Miamii colloids	A_1	12.8
	A_2	11.3
	B	7.8
	C	4.3
Napanee	C	2.0
Napanee colloids	C	5.50
1 soil		6.7
1 colloid		10.3
Unindentified clay loams:		
2 soils		6.5
2 colloids		15.8
3 soils		4.4
3 colloids		7.4
Fuller's earth		12.4

The water removed from the sugar solution by the surface horizon of several organic deposits exposed to three temperatures, was determined. The data in table 2 show that the soils are able to absorb water from the sugar solution and make it unfree or inactive. In addition, considerably more water is removed from the sugar solution by the samples when maintained at tempera-

tures higher than those that exist in the laboratory. When expressed on the oven-dry basis or 100°C., the amount of water so held ranges from about sixteen to more than twenty per cent in case of the air-dry soils, and from about twenty-six to more than thirty-five per cent after the soils have been exposed to 100°C. These are striking figures. Similar results were obtained with mineral soils as shown by the data in table 4.

The water taken from the sucrose solution by samples of Fuller's earth and several mineral soil horizons as well as the colloids extracted from some of them was determined. According to the data in table 3 differences exist with respect to the various horizons of a given profile. The B horizon of the Ontonagon soil removes more water from the sugar solution than do the A_1, A_2 and C horizons but the corresponding horizon in the Miami soil takes out less than the A_1 and C horizons. The activity of the colloids extracted from a given horizon is much greater than that of the untreated samples. This property decreases from horizon A_1 downward. The unidentified samples are rather active in this respect.

TABLE 4

Water removed from sucrose solution by several soil horizons exposed to different temperatures and probably made unfree or inactive

SOIL TYPE	HORIZON	TEMPERATURE		
		100°C.	55°C	Room temperature
Ontonagon	A_1	2.5	...	1.5
	A_2	2.6	...	2.1
	B	3.5	...	1.3
Colloids	B	6.5	...	...
	C	2.3	...	1.2
Miami colloids	A_1	12.8	11.8	8.2
	A_2	11.3	7.7	5.0
	B	7.8	4.7	4.3
	C	4.3	2.8	2.7
Miami	A_1	2.9	2.2	1.9
	A_2	1.9	1.0	1.6
	B	2.1	2.1	1.4
	C	2.4	1.4	1.3

The foregoing results, therefore, as well as those of McCall et al (5) point strongly to the theory that soils are capable of holding appreciable amounts of water in such a condition that it does not function as a solvent. It is made unfree. This water seems to be both physically adsorbed and chemically combined.

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SELECTIVE ABSORPTION OF IONS BY SEEDS[1]

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In a series of publications on the effect of seeds on ion absorption, it has been pointed out that seeds in salt solutions and in mineral and organic acids, change the hydrogen-ion concentration of these liquids; moreover, different seeds can change the H-ion concentration of the solutions to definite points, and a certain equilibrium is reached in all salt solutions or acids after the seeds have been immersed sufficiently long. The results published thus far show that seeds placed in an acid solution will decrease the free hydrogen ions to a definite pH value, and seeds in alkaline solutions will bring the pH value of the solutions down to the same definite point for each kind of seed. Each kind of seed changes all dilute acids and salt solutions to the same characteristic point, and an equilibrium is reached with decreasing rapidity after a definite time. In an earlier publication (2) the statement was made that the chemical properties of the chief protein content of the seeds seemed responsible for the changes in H-ion concentrations.

If the results obtained with the different basic salt solutions and acids are plotted, smooth curves can be constructed. It might be expected that acid salt solutions, like KH_2PO_4, or solutions of K_2HPO_4 when sufficiently weak would behave differently in the course of reaching their final equilibria. Differential ion absorption can readily be demonstrated in such solutions, in spite of the fact that an equilibrium is finally reached.

Aluminium salts have been for a long time of great interest to soil scientists and botanists on account of their possible effect on germination and plant growth. If seeds are immersed in certain salt solutions, of which aluminum salts are representative, the pH values are first lowered and after some time changed to a much higher pH value than the original salt solutions.

METHODS

Among a large number of different salt solutions, stock solutions of 1/175 *N* aluminum sulfate and 1/170 *N* aluminum nitrate were prepared. The stock solutions were sufficient to repeat the experiments a number of times. For convenience two large seeds were selected. Series of 50 dent corn and 50 soybeans were placed in bottles containing 100 cc. of solution; 1.8-cc. solutions

[1] Paper No. 245 of the Journal series, New Jersey Agricultural Experiment Stations, Department of Soil Chemistry and Bacteriology.

were pipetted off after definite time intervals, and the H-ion concentrations of the solutions determined colorimetrically.

RESULTS

The results for the aluminum solutions are given in table 1 where the initial pH values are compared with the readings at definite time intervals.

The lowering of the pH values was very rapid, followed by a decrease in the rate of change to higher pH values. It took but 3 minutes for soybeans to change the $Al(NO_3)_3$ solutions from pH 4.5 to 3.6 and 12 minutes from 3.6 back to 4.5, while after 60 minutes the H-ion concentration was changed to pH 5.8. The salt solutions remained at this pH value for the following 18 hours. Increasing the time to 48 hours did not change the equilibrium reached. The changes produced in the $Al_2(SO_4)_3$ solutions were not so marked but

TABLE 1

Effects of seed immersion on pH values of aluminum solutions

	ALUMINUM SULFATE 1/175 *N*		ALUMINUM NITRATE 1/170 *N*	
	Corn	Soybeans	Corn	Soybeans
	pH	*pH*	*pH*	*pH*
Initial	4.7	4.7	4.5	4.5
30 seconds	4.3	4.5	4.2	4.3
1 minute	4.2	4.3	3.9	3.9
2 minutes	4.1	4.2	3.6	3.7
3 minutes	4.1	4.1	3.6	3.6
5 minutes	4.1	4.3	3.6	3.6
7 minutes	4.15	4.6	3.65	3.8
10 minutes	4.2	4.9	3.7	4.2
15 minutes	4.2	5.1	3.9	4.5
20 minutes	4.2	5.4	4.0	4.9
30 minutes	4.3	5.6	4.2	5.4
60 minutes	4.3	5.8	4.3	5.8

followed the same course. This phenomenon is illustrated graphically in figure 1. The changes produced by corn were less but the phenomena were practically the same.

It would seem that the differential absorption of ions if greatly influenced by the amphoteric character of the proteins present in the seeds, and the difference between the total and the rate of absorption in corn and soybeans can be attributed to the difference in protein contents of these seeds. Hoagland, Davis, and Martin (1) studying the fresh water alga *Nitella clavata* found that the absorption of various ions was determined by a variety of conditions in the culture medium. Nearly all the inorganic elements found in the cell sap were present in dissociated form, and nitrate penetrated more rapidly from a slightly acid solution than from an alkaline solution.

The curve in figure 1 seems to indicate that nitrate ions are removed at a

faster rate than the sulfate ions. In aluminum nitrate and aluminum sulfate solutions the dissociated cations are removed first and then the anions.

Data at hand show that the rate of absorption is influenced by the concentration of the salt solutions. This might be expected.

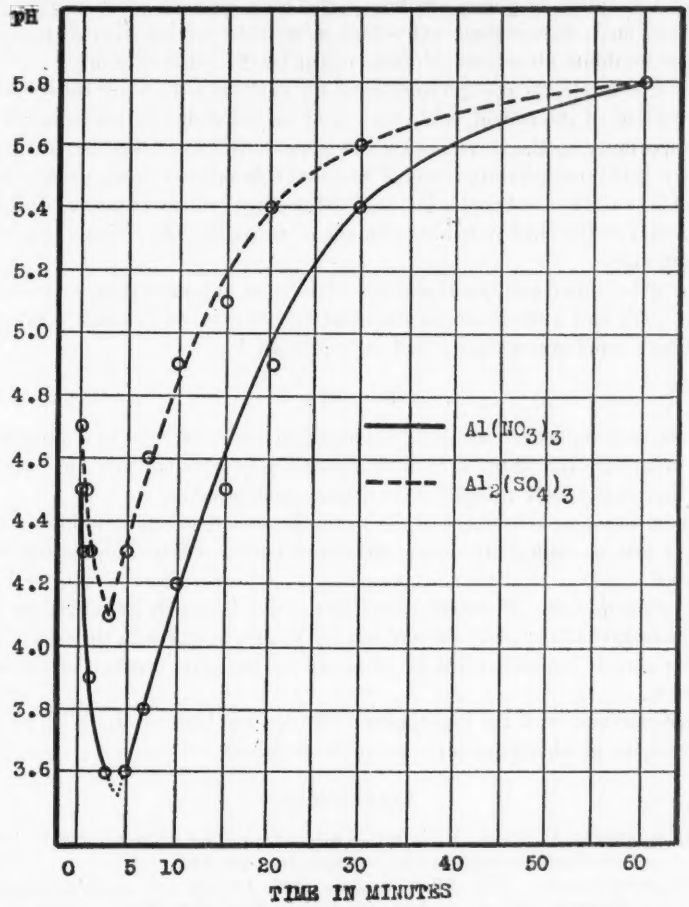

FIG. 1. EFFECT OF SOYBEAN IMMERSION ON ALUMINUM NITRATE AND ALUMINUM SULFATE SOLUTIONS

The fact that (*a*) different ions are absorbed by seeds in succession at a fast rate, (*b*) an equilibrium is established after a comparatively short time, and (*c*) the rate of absorption is influenced by the concentrations of the salt solutions, tends to show that the amphoteric character, amount and kind of protein material present are important factors in differential absorption of ions.

It is well known that aluminum salts are able rapidly to flock out colloidal material in suspension, and that these salts in weak concentrations have a high precipitation power for proteins. In view of the fact that differential absorption takes place in the seeds, and assuming that a similar phenomenon might take place in young seedlings although a growing plant might have different final characteristic pH points, a possible precipitation of proteins caused by dilute aluminum solutions might be the cause of injury.

Since, as a rule, the precipitating agent for a colloid is the ion of the opposite sign to that of the colloid, while the ion of the same sign as the colloid is of no importance in the precipitation but appears to exert an antogonistic influence to the precipitating action of the ions of the opposite sign, it seems very possible to add to a nutrient solution or soil medium sufficient material with the same sign as the chief proteins to oppose or neutralize the action of the aluminum salts.

Results of differential ion absorption of different vegetable proteins found in these seeds and a discussion of the observed phenomena in connection with Donnan's equilibrium theory will be published later.

SUMMARY

Corn and soybean seeds were immersed in two representative aluminum salt solutions, the changes in hydrogen-ion concentration and the rate of reaction change were recorded after definite time intervals.

There was a rapid lowering of pH values in the salt solutions, followed by a slower rate of change to higher pH values until a definite equilibrium was reached.

It seems that the differential absorption of ions is greatly influenced by the amphoteric character, amount and kind of proteins present in the seeds.

The rate of ion absorption is influenced by the concentration of the salt solution.

In connection with the experiments recorded the high precipitation power for proteins of aluminum salts is briefly discussed.

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